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COLLOID & CAPILLARY CHEMISTRY

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TRANSLATED FROM THE THIRD GERMAN EDITION BY

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WITH 157 DIAGRAMS

NEW YORK

E. P. DUTTON AND COMPANY, INC.

PUBLISHERS

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PRINTED IN GREAT BRITAIN

AUTHOR'S PREFACE

IN writing the first edition of this book, I was guided by the following idea. If we start from certain general points of view, we are able to see more clearly what may be regarded, on the basis of available work, as cultivated territory, what we have to regard as untouched ground, and where we may commence to dig with the best prospect of success. The prominence given to general points of view made it necessary to deal with Capillary Chemistry at length; for Colloid Chemistry deals with very complicated systems, and the laws governing the phenomena (adsorption, influence of solubility, electrical effects) cannot be developed so easily as in connexion with the simpler systems of Capillary Chemistry. These systems form a necessary basis, upon which Colloid Chemistry can be more easily built up.

In the second edition I was guided by the same idea; a thorough reconstruction and extension were, however, necessary. In recent years abundance of new data has been collected, and it also appeared to be advisable to treat of the processes of crystallization, and, more generally, of the formation of new phases, and of molecular motion, in special sections, in order that the book might be justified in bearing the title of a Colloid Chemistry. Capillary Chemistry continues to take up a large share of space. This is due to the fact that other expositions of this subject do not exist, while they are to be had for crystallization and for molecular motion. I hesitated, therefore, to shorten the sections dealing with the measurement of surface tension, etc., which would have otherwise been justifiable, and more in accordance with the scope of the whole work.

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DAHLEM, *January*, 1922
KAISER WILHELM INSTITUTE
FOR PHYSICAL CHEMISTRY

78197

PUBLISHERS' NOTE

THE manuscript of the present translation was in the first instance prepared by Dr. H. S. Hatfield from the second German edition. Additional matter, appearing in the third German edition, was subsequently added, so that the present English edition is entirely up-to-date.

The translator desires to acknowledge the assistance of Dr. J. Chadwick and Mr. C. D. Ellis, of Cambridge, Dr. E. Higgins, of Liverpool, and Mr. B. W. Holman, of the School of Mines; he is greatly indebted to his wife for assistance which has saved much time and labour.

The publishers are also indebted to Dr. E. Stedman, of Edinburgh University, who has translated the addenda and seen the whole work through the press. The care which he and others have bestowed on the work has, it is hoped, resulted in an accurate and intelligible rendering of the original. The publishers are further indebted to Professor G. Barger, of Edinburgh, for advice on numerous points.

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INTRODUCTION

In his investigation of diffusion in aqueous solution, Thomas Graham[1] in the year 1861, distinguished between two groups of substances. Those of the one group, such as glue, proteins, silicic acid, and others, diffused slowly or not at all through parchment paper and animal membranes; when their solutions were evaporated, they separated in the form of amorphous jellies or flakes. He called these substances "colloids," glue-like, from ἡ κόλλα, glue. Substances of the second group, such as salts, sugar, etc., diffused quickly through the membranes in question and separated from their solutions in crystalline form. He termed them "crystalloid." As easily happens when a principle of order is successfully applied to a set of phenomena hitherto unordered, Graham believed that a sharp line of division separated the two groups; he believed this even more firmly when he realized that colloids play an important part in the structure of living beings.

The solutions of colloidal substances, known as colloidal solutions or *sols*, had already been the objects of extensive investigation before Graham's time. Indeed, alchemists and iatro-chemists worked by preference with the body fluids, which are almost exclusively colloidal solutions, so that they had necessarily collected certain experimental data concerning them. In this connexion we may recall the alchemistic experiments with silicic acid jelly, which Goethe describes in "Dichtung und Wahrheit." Selmi [2] had, from the year 1844 onwards, investigated colloidal solutions of sulphur, Prussian blue, and other substances, and recognized clearly several ways in which their behaviour differs from that of ordinary solutions. To Faraday [3] we owe a valuable research on gold sols, published in 1857, after Jeremias Benjamin Richter [4] had already, in 1802, gone far towards elucidating the nature of purple of Cassius and the gold sols. But Graham was the first to name and characterize this set of phenomena.

In the decades which followed Graham's work, the experiments of van Bemmelen, H. Schulze, Carey Lea, and others, brought to light many properties of colloidal structures. But nothing was actually found which contributed fundamentally and directly to the elucidation of their nature. A change was brought about when the theory of solutions was developed in the last years of the nineteenth century. The question then arose: Are colloidal solutions solutions in the true sense, is the dissolved substance divided, as in the case of ordinary solutions, down to its molecules, and is their large size the cause of the slow diffusion and the feeble tendency

[1] Phil. Trans. **151**, 183 (1861); Lieb. Ann. **121**, 1 (1862).
[2] See *Guareschi*, Kolloidzeitschr. **8**, 113 (1911).
[3] Phil. Trans. **147**, 154 (1857).
[4] See *W. Ostwald*, Kolloidzeitschr. **4**, 5 (1909).

to crystallization? Or do colloidal solutions contain particles which, although built up of many molecules, are still too small to be seen by the microscope?

The question was answered in 1903 by Siedentopf and Zsigmondy.[1] The ultramicroscope invented by them extended the limit of visibility of particles from about 500 $\mu\mu$ down to about 10 $\mu\mu$. It then became evident that many colloidal solutions were optically resolvable, and contained particles, visible ultramicroscopically, with diameters between 10 and 500 $\mu\mu$. In the case of these sols, therefore, the division did not extend down to the molecules; each single particle consisted of a large number of molecules. This did not exclude the existence of colloidal solutions the particles of which might consist of one very large molecule: indeed, such limiting cases are known.

In the discussion of this question of the nature of colloidal solution, the conception of a colloid had undergone a change almost unperceived. Chemists no longer spoke, as Graham had done, of two groups of substances, "which appear to be different worlds of matter, and lead to a corresponding division of chemistry."[2] For the colloidal solutions of the metals were the especial objects of investigation, and the metals can crystallize excellently, and nevertheless give colloidal solutions. The concept "colloid" no longer characterized particular substances, but rather a particular state, as does, for example, the concept "dissolved." By the colloidal state was understood the extremely intimate mixture of two phases, in which, however, the scattered phase is not necessarily divided down to its molecules, but only into particles visible ultramicroscopically and having, therefore, diameters of 500 $\mu\mu$ and less. Of the two properties used by Graham to characterize the concept colloid, slow diffusion and separation in amorphous form, only slow diffusion was necessarily associated with this newly defined colloid state, and not separation in amorphous form. For, according to this definition, it is not impossible for a colloidal solution to contain very fine crystals, which separate as coarser crystals. Conversely, according to Graham a pure glass might be described as a colloid; this was indeed occasionally done. According to the new definition it was excluded; for such a glass is a homogeneous phase, and therefore not colloid. Glass, as an amorphous solid, is rather to be contrasted with the crystalline solids.

This changed view of the concept "colloid" is to be found plainly stated here and there in the papers of Zsigmondy[3] and of others[4]; frequently it may be read between the lines as an unexpressed assumption. It was not therefore new when it was emphasized very decidedly by von Weimarn[5] in 1907, although perhaps as yet less well known to biologists.

A useful extension of our concepts is due to Wo. Ostwald.[6] A structure consisting of two phases, one being distributed intimately and uniformly throughout the other, he called a *disperse system*. He suggested the terms

[1] Ann. der Physik (4), **10**, 1 (1903).

[2] Lieb. Ann. **121**, 68 (1862). On p. 293 of the Phil. Trans. paper (l.c. p. 1) Graham says: "In the so-called blood crystals of Funke, a soft and gelatinous body is seen to assume a crystalline contour. Could any facts more strikingly illustrate the maxim that in Nature there are no abrupt transitions, and that distinctions of class are never absolute?" (Trans.)

[3] E.g. Zeitschr. für Elektrochemie, **8**, 684 (1902); further, "Zur Kenntnis der Kolloide," Jena, 1905, p. 170 *et seq.*

[4] E.g. *Rohland*, Kolloidzeitschr. **1**, 201 (1907).

[5] Kolloidzeitschr. **2**, 76 (1907).

[6] Kolloidzeitschr. **1**, 291 (1907).

coarsely disperse, when the particles of one of the phases could be discerned when with the naked eye or with the microscope; and *colloidally disperse*, when the ultramicroscope was required to effect resolution. A true solution, which behaves in all its properties as a homogeneous phase, may be described as *molecularly disperse*, although there are certain objections to this (cf. p. 532). The transitions from coarsely disperse to colloidally disperse, and from colloidally disperse to molecularly disperse, are perfectly continuous.

The two phases of a disperse system play, as a rule, different parts. One is continuous; the surfaces which it has in common with the other phase are concave, as in the case of the liquid phase of a sol. This phase is called the *dispersion medium*. The other phase has a closed surface, the boundary surfaces are convex, as in the case of the particles in a colloidal solution; this phase is called the *disperse* phase. If we form all possible combinations of two phases, the one first named being the dispersion medium, and the second the disperse phase, and if no sharp line be drawn between coarsely and colloidally disperse systems, we arrive at the following scheme:

Gaseous—liquid	Mist.	
Gaseous—solid	Smoke.	
Liquid—gaseous	Foam.	
Liquid—liquid	Emulsion	(If colloidally disperse sol or sometimes gel.):
Liquid—solid	Suspension	
Solid—gaseous	Solid foam.	
Solid—liquid	Solid emulsion[1]	(If colloidally disperse: solid sol.)
Solid—solid	Solid suspension	

If we desired to be perfectly consistent, we ought really to describe the chemistry of coarsely and colloidally disperse systems as *dispersoid* chemistry. But colloidally disperse structures, and particularly those with a liquid dispersion medium, preponderate to such an extent, by virtue of their great stability and consequent frequency and importance, that the science of the chemical and physico-chemical properties of coarsely and colloidally disperse systems may usefully remain designated by the term *colloidal chemistry*. When the word disperse is used, it will include the concepts coarsely disperse and colloidally disperse; molecularly disperse is not included.

A property which distinguishes all disperse structures is the extraordinary size of the interface between the two phases. As a necessary consequence of this fact, all physical and chemical phenomena which depend upon the existence of an interface become very prominent in disperse systems. The science of the physical properties of interfaces as connected with their material properties is called *capillary chemistry*.

Capillary chemistry is therefore a necessary foundation for colloid chemistry. The term capillary chemistry is not quite a happy one; an expression meaning "chemistry of interfaces" would be more to the point. For the word capillary suggests processes in liquid media. But capillary chemistry is to include the science of processes taking place at interfaces between all pairs of phases of the foregoing scheme.

Closely connected with capillary chemistry, but independent of it in

[1] The *jellies* or *gels* were at one time fairly generally regarded as solid emulsions. But in the case of many of them it is now practically certain that this is not the case, but that they are to be regarded as a special kind of suspension (cf. p. 659).

essential points, is the question as to the conditions under which a phase appears or is transformed into another phase. The factors upon which the formation of a new phase under conditions of undercooling or supersaturation depends, are of importance in the production of the majority of colloidal structures. This again leads us to the discussion of the solid-amorphous state and its importance for sols, gels, etc. For although the amorphous form of separation does not enter into the definition of the concept of a colloid, it is nevertheless not a matter of chance that the particles of a colloid solution are to so large an extent not crystalline but amorphous-solid.

It is a peculiarity of colloidal chemistry that it may be entered as it were, through two gates. We may start from a simple system of two phases with a small common boundary surface, and imagine the one phase divided more and more finely and distributed throughout the other, with corresponding increase of the interface. Capillary chemistry collects its data at the interfaces of simple systems, and applies these data to disperse structures. But we may also start from pure solution, from the "molecularly disperse" system, and imagine its particles continually increased until we come into the region of colloid chemistry. When the ultramicroscope taught us to regard sols as two-phase structures it was at first believed that a sharp line of division had been found between the colloidal solution, a two-phase system, and the true solution, a single-phase system. What was so distinctive of true solution, namely osmotic pressure and the phenomena connected with it, was thought to be necessarily absent in the case of colloidal solutions. It came as a surprise when Einstein[1] and von Smoluchowski[2] showed that the kinetic theory of gases leads to quite a different view. As far back as the year 1827, the English botanist R. Brown[3] had described the irregular trembling motion of the particles of a suspension as seen under the microscope. Under the ultramicroscope this Brownian molecular movement was still more prominent in the case of the particles of a sol. Einstein and von Smoluchowski came to the conclusion that this motion is caused by the impacts of the molecules of the liquid upon the particles, and that each particle must then move as if it were a single large molecule. Svedberg,[4] and especially Perrin,[5] completely confirmed this theory. From measurements under the microscope of the Brownian movement of the particles of a coarsely disperse system, it is possible to calculate the value of the constant R of van't Hoff's equation

$$P.V = R.T$$

The theory of the Brownian movement is a further necessary condition for the understanding of disperse systems.

The first part of this book will therefore deal with the physico-chemical foundations of colloid chemistry, that is to say, with capillary chemistry, the formation and interconversion of phases, and molecular motion. Upon these three foundations colloid chemistry itself will be built up in the second part of the book.

[1] Ann. der Physik (4), **17**, 549 (1905).
[2] Ann. der Physik (4), **21**, 756 (1906).
[3] Phil. Mag., **4**, 101 (1828); **6**, 161 (1829). Both papers were reprinted in the author's collected works by the Ray Society, 1866. The second paper mentions earlier descriptions of the same phenomenon by other writers.
[4] Nov. Act. reg. soc. scient. Upsal. (4), **2**, Nr. 1 (1907).
[5] Compt. rend. **146**, 967 (1908); **147**, 530 (1908); Ann. de. chim. et de phys. (8), **18**, 5 (1909).

THE PHYSICO-CHEMICAL FOUNDATIONS OF COLLOID CHEMISTRY

A. CAPILLARY CHEMISTRY

CAPILLARY CHEMISTRY falls into natural divisions according to the kind of interface at which the various possible pairs of phases meet. We have to distinguish the following interfaces:

Liquid—gas.
Liquid—liquid.
Solid—gas.
Solid—liquid.
Solid—solid.

The surface tension, a quantity characteristic of the interface, and its relation to the chemical properties, must first be discussed for each pair of phases. On account of the complete rigidity of the interface solid—solid, almost all phenomena appertaining to this pair are missing, and hence little can be said at present under this heading. On the other hand, the *capillary-electrical* processes in the widest sense are of great importance, and they will be treated in a fifth division; in a sixth the question of the thickness of boundary layers will be dealt with.

I. The Interface Liquid—Gas

Surface Tension and Free Surface Energy

It is a long-known phenomenon, of everyday occurrence, that a liquid left to itself in a gas space, assumes the form of a drop and thus tends to be spherical. Segner,[1] however, and more clearly Th. Young,[2] were the first to draw from this simple fact conclusions which led to physically well characterised quantities.

A sphere has minimum surface area for a given volume. Liquids must therefore have a tendency to diminish their surface as much as possible. This suggests the idea that every space filled with liquid is, as it were, enclosed in an elastic membrane, the tension of which causes the reduction in the surface. We thus arrive at the conception of *surface tension*, a force acting across a certain length, and tending to reduce the surface. The dimensions of surface tension are therefore $\frac{\text{force}}{\text{length}}$ or in the usual symbols $M.T.^{-2}$

It is important to note from the outset that surface tension differs

[1] Communic soc. reg. scient. Götting., **1**, 301 (1751).
[2] Phil. Trans. **95**, 65 (1805).

fundamentally from the tension of an elastic membrane, such as a stretched piece of rubber, in one important respect. In the case of a pure liquid, the surface tension is completely independent of the size of the surface. It does not therefore alter, if the surface is increased, whereas the tension of an elastic membrane depends upon the extent to which it is stretched.

Since, on account of the surface tension, every liquid automatically diminishes its surface, an increase of the surface requires work to be done. This work is the *surface work* or *free surface energy.* We speak of free surface energy, and not simply of surface energy, because the free surface energy just defined is not the total energy which is expended in producing a new surface, but only the mechanical work which is required for this.

The total surface energy also includes, besides this mechanical work, the quantity of heat which has to be supplied, since the surface cools itself in this process of enlargement (cf. p. 35).

The connexion between the concepts surface tension and free surface energy becomes quite clear according to Maxwell's exposition.[1] We imagine a wire CABD (Fig. 1) bent into a ∩-shape, upon which a second wire CD can slide without friction. The arrangement is vertical. In the rectangle ABCD is a lamella of soap solution, which tends to contract and so lift the movable wire CD. If the latter be loaded with weights, it is possible to find a weight at which the wire CD will stay at any position, corresponding to any size of lamella, (within limits,) while a smaller weight is pulled upwards, and a greater one tears the fully extended lamella. This particular weight, therefore, just balances the surface tension of the lamella, and it corresponds to double the surface tension of the latter, since both surfaces are effective.

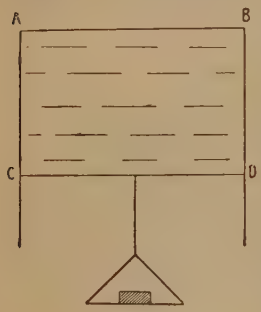


Fig. 1.

If we now pull down the movable wire loaded with this weight from a position quite close to AB to the position CD, we do work against the surface tension; this work, and therewith the free surface energy, is obviously the greater, the greater on the one hand the adjusted weight, and, on the other, the surface ABCD. Hence

Free surface energy = surface tension × area of surface,

$$A_\omega = \sigma\omega.$$

From this equation it follows that

$$\sigma = \frac{A_\omega}{\omega}.$$

We may therefore regard *the surface tension as the free surface energy per unit of surface*; in other words, it is numerically equal to the *mechanical work which must be done in generating unit surface.*

The surface tension is therefore defined according to its dimensions as $\frac{\text{energy}}{\text{surface}}$.

In the following pages, the force in dynes acting across unit length

[1] Scientific Papers, Cambridge, **2**, 552 (1890).

$\left(\frac{\text{dynes}}{\text{cm.}}\right)$ will be taken as the unit of surface tension, or in general of any interfacial tension.

In the experiments described above, the soap-solution lamella was introduced for the sake of illustration. As we shall see later (p. 794), this would in reality behave upon extension otherwise than as we have assumed. In the case of a lamella of a pure liquid—not a solution—immersed in its own vapour, the experiments would take place as described. In every case, the following considerations apply fundamentally to a liquid which is in contact with its own vapour.

Surface Tension and the Theory of the Liquid State

The previous discussion made no assumptions regarding the properties of the liquid state. Now the question as to the shape which spaces filled with liquid in general assume, has mostly been treated in another way, which was first adopted by Laplace [1] with especial success, his treatment being revised and enlarged in the course of the nineteenth century. In this connexion various peculiarities of the liquid state are assumed, from which the conditions of the minimum of surface, the existence of a surface tension, and other consequences can be deduced. In this way we not only arrive in a simple manner at equations which describe the shape of a space filled with liquid, but our attention is also directed to certain quantities connected with the surface tension, which lead to new relations capable of being investigated experimentally. We will now briefly consider these questions.

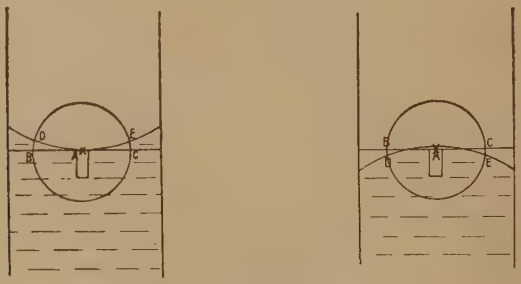
A case, in which the properties of a liquid which determine its shape appear very noticeably, is the rise of water in capillary tubes, a phenomenon which was already known to Leonardo da Vinci, and from which the majority of early theoretical investigations started. It naturally occurred to the successors of Newton in the eighteenth century to explain the rise in capillary tubes by an attraction proceeding from the liquid meniscus or the walls of the tube. Clairault, who was the first to study closely the quantitative side of the question, assumed an attractive action of the walls, and searched in vain for a form for the attraction function which would describe correctly the dependence of the height of rise upon the diameter of the capillary. But when Hawksbee showed that the capillary rise with equal diameter of the capillaries is independent of the thickness of the wall, the idea suggested itself that the attractive force between the particles of the wall and those of the liquid, and also between the particles of the liquid itself, is only active over very short distances, and Laplace then developed this idea and showed how, upon the basis of this simple assumption, we may actually arrive at equations which describe correctly not merely the rise in capillaries, but also the whole complex of the properties of the liquid which determine its shape.

The liquid state is thus distinguished by the fact that in it the molecules are pressed more closely together and that therefore the attraction between them, which acts only over very short distances, makes itself felt, while it does not take effect in gases when they are sufficiently tenuous. In the interior of the liquid the forces acting in different directions upon a molecule cancel one another, but the layer of liquid which lies next the gas space is pulled inwards with a definite pressure by the resultant of the

[1] Mécanique céleste, Supplém. au livre **10**, 1 (1806); Œuvres, **4**, 389 (1845).

unbalanced attractive forces. It at once follows from this that the surface is reduced to a minimum, for work must be expended to bring liquid from the interior to the surface.

Laplace considers the attraction which a liquid with a curved surface exerts upon a minute column of liquid situated at a point of the liquid surface and extending into the interior of the liquid. From what we have just said the attraction must only be effective over very short distances. The attraction upon the point A (Fig. 2) of this column of liquid is caused only by the molecules of liquid which are within the range of attractive power, that is to say, within a sphere the radius of which is the so-called *radius of molecular attraction*. In Fig. 2 *a* and *b*, the circle drawn around A as centre indicates this sphere. The attraction acting at A on the unit of surface may be taken as made up of two parts: first, the attraction which the whole liquid lying below BAC exerts; this is the pressure with which A would be drawn inwards, if it were in a plane surface. This pressure is the so-called *internal pressure* K. But in the case of a *concave* liquid surface, the mass of liquid BACED above BAC attracts A upwards (see Fig. 2 *a*). The attraction due to this cause is greater, the greater the



a FIG. 2. *b*

curvature of the surface. The expression which gives this action is therefore inversely proportional to the radius of curvature of the surface. Accordingly the second part of the attraction is equal to the so-called *surface pressure* $\frac{H}{R}$. This must be subtracted from the internal pressure, since it acts in the opposite direction. The total attraction is therefore equal to

$$K - \frac{H}{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In the case of a *convex* surface having the same curvature we must remember that the space CABDE is not filled with liquid. If it were, the molecules which are contained in it would cause a part of the pressure K, and they would, on account of their position, attract the column of liquid upwards. As this space is not filled with liquid, the pressure downwards is by just so much the greater as the attraction $\frac{H}{R}$ of molecules in this space would be in an upward direction. The total attraction is therefore

$$K + \frac{H}{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It is clear that the surface pressure $\frac{H}{R}$ must act like the force exerted by an elastic membrane surrounding the liquid. For the molecules of liquid which contribute most to $\frac{H}{R}$ lie very close to the point A on the surface. That H has the character of a tension follows from dimensional considerations. K as a pressure has the dimensions $ML^{-1}T^{-2}$; since $\frac{H}{R}$ has like dimensions, H has the dimensions MT^{-2}; that is, H is a tension (cf. p. 5). As we shall see later (p. 20), $\frac{H}{2}$ turns out to be equal to the surface tension σ. We must carefully distinguish between the *surface pressure* $\frac{H}{R}$, which depends upon the radius of curvature, and the *surface tension* σ, which is completely independent of the curvature.

In view of matters to be discussed later, it is important to find out in what relation K and H stand to other quantities, such as the radius of the sphere of molecular action, and the density of the liquid. We get, according to Laplace, the following expressions:

$$K = 2\pi\varrho^2 \int_0^\infty \psi(x)dx = 2\pi\varrho^2 \int_0^\delta \psi(x)dx, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$H = 2\pi\varrho^2 \int_0^\infty x\psi(x)dx = 2\pi\varrho^2 \int_0^\delta x\psi(x)dx \, . \quad . \quad . \quad . \quad . \quad (4)$$

Here ϱ denotes the density of the liquid, $\psi(x)$ a function giving the dependence of attraction upon distance. The length of x only extends to the very small distances over which the attraction is effective. Its limit is the radius of molecular attraction δ.

If the liquid has a curvature of any form with the two principal radii of curvature R_1 and R_2 we get in general for a column of liquid directed into the interior of the liquid a pressure

$$K + \frac{H}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Here we must ascribe negative values to the radii of curvature, if they belong to a liquid surface, which is concave to an observer outside the liquid.

The two quantities K and H (or σ) characterize the liquid state and determine the properties of the various liquids. They stand in a curious relation to one another. σ is a small quantity (in the case of most liquids between 20 and 100 dyne centimetres); the pressure exerted by it does not change the volume sensibly. On the other hand it determines decisively the form of the liquid surface, since liquids are mobile. It may therefore be measured by very many different methods.

K has, on the contrary, a very large value. This follows from the fact that, according to equation (3), we can get the differential

$$dK = 2\pi\varrho^2\psi(x)dx$$

from the differential

$$dH = 2\pi\varrho^2 x\psi(x)dx$$

by dividing dH by the very small quantity $x = \delta$. The estimated values of K amount to 1,000 and more atmospheres. Although the internal pressure determines the volume of the liquid, and we should therefore like to introduce it as a particularly important variable, it has not hitherto been found possible to measure it directly and reliably. In all measurements of surface tension it cancels out ; the surface tension alone determines the form which a quantity of liquid takes under given external circumstances.

The fact that the internal pressure makes itself felt qualitatively in various processes is, however, also important for the phenomena of capillary chemistry. It appears directly in all experiments, in which we do not permit the particles of a liquid to slide past one another, but attempt to separate them absolutely from one another, that is to say, to increase the volume of the liquid by tension. If we succeed in giving a liquid a larger volume than it has naturally under the particular conditions of temperature and pressure, the internal pressure makes itself felt in the striving of the liquid to assume its correct volume. The breaking-strength of a liquid, its true cohesion, is a measure of the internal pressure.

J. Meyer [1] has described fully such experiments. For the present only the following experiment made by M. Berthelot [2] will be given. A thick-walled tube is filled as completely as possible with a liquid and its vapour, and by warming the liquid is made completely to fill the tube. If we now cool the whole, it may easily happen, if the wall of the tube was thoroughly clean, and all chance air-bubbles had been completely dissolved, that the tube remains completely filled at low temperatures. Vibration or excessive fall of temperature will cause the liquid to resume with a snap its proper volume.

The value of K may be calculated directly from the equation of van der Waals[3]

$$\left(p + \frac{a}{v^2}\right)(v - b) = R\mathrm{T}.$$

For the quantity $\frac{a}{v^2}$, which has to be added to the external pressure on account of the molecular attraction, is none other than the internal pressure K. a is the specific molecular attraction, which is not dependent upon the density. Since a and b may be deduced from the critical constants of the vapour, K is got by dividing a by the square of the specific volume of the liquid. The values of K, which van der Waals thus calculated, were, for example, at 0°, and atmospheric pressure for

Ether	1,400	atmospheres.
Alcohol	2,400	,,
Water	11,000	,,

Although the theory of van der Waals does not in general accurately represent the behaviour of liquids, we may regard it as certain that the internal pressure is of this order of magnitude.

Since the surface tension, as follows from equations (3) and (4), is closely related functionally to the internal pressure, the dependence of the

[1] Abh. d. deutsch. Bunsengesellsch. Nr. 6. There also the older literature will be found. According to *Budgett* [Proc. Roy. Soc. **86**, 25 (1912)] the great firmness with which highly polished steel plates adhere to one another arises from the fact that films of water are present between them, whose breaking-strength has to be overcome.

[2] Ann. de chim. et de phys. (3), **30**, 232 (1850).

[3] The constant of the equation is denoted by R and not by R in order to indicate that the gram and not the molecule is taken as unit of quantity.

urface tension upon the nature of the liquid is often similar to the dependence f the internal pressure, although frequently distorted in form (cf. p. 42).

In contrast to the volume-reducing tendency of the internal pressure tands the volume-increasing tendency of the *heat-pressure*, and the equili- rium volume of the liquid is determined by the interaction of the two. n van der Waals' equation, the heat-pressure is given by the expression $\frac{RT}{v-b}$. According to the kinetic theory of gases and liquids, it is caused by the motion of the liquid molecules.

The probable magnitude of the radius of the sphere of molecular action δ will be discussed below (p. 307). Here need only be mentioned that we shall assume in what follows that δ is a multiple of the diameter of the molecules, and will thus have as a rule a length of several $\mu\mu$.

This is not the place to discuss how Laplace's theory of surface tension developed in the course of the century, and what are its defects.[1] Only the following need be noted. Laplace assumes that the density of the liquid remains exactly the same, and at a plane liquid surface there exists for him only an internal pressure, and not a surface tension. Although his theory explains the physical phenomena sufficiently as a rule, it none the less fails in many cases. It does not give correctly, for example, their dependence upon the temperature in the neighbourhood of the critical point (cf. p. 29). If we wish to describe capillary phenomena upon the basis of a general theory of liquids, it is better to employ the theory of capillarity worked out by van der Waals[2] and his pupils, particularly Hulshof[3] and Bakker.[4]

The idea which was developed by these investigators is this, that the density of the liquid is not constant, but gradually passes into that of the gas at the boundary layer. Hulshof especially showed that this supposition alone suffices to prove that at every interface—including a plane one—a surface tension must exist, provided that we assume an internal pressure. For then the pressure in the surface layer parallel thereto must be greater than that in the perpendicular direction. An excess of pressure parallel to the surface remains, which causes the surface tension. We get for the surface tension the equation already deduced by van der Waals by another method.

$$\sigma = k \int \left(\frac{d\varrho}{dh}\right)^2 dh \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which k is a constant' $\frac{d\varrho}{dh}$ the gradient of density in the surface layer; the tension therefore increases with the gradient of density. It is further

[1] See, among others, *van der Waals—Kohnstamm*, Lehrbuch der Thermodynamik, **1**, 253 (1908); further. for a comprehensive exposition of the mathematical-physical side of this subject, *Minkowski*, Kapillarität [Enzyklopädie d. Math. Wissenschaften, **5**, 1, Heft 4, p. 558 (1907)]. [The best exposition in English is the article "Capillary Action" in Encyclopædia Britannica, written by Maxwell for the 9th Ed. and revised by Rayleigh for the 10th. (Trans.)]

[2] Zeitschr. f. physik. Chemie, **13**, 657 (1894).

[3] Ann. d. Physik (4), **4**, 165 (1901).

[4] Zeitschr. f. physik. Chemie. **28**, 708 (1899); **33**, 475 (1900); **34**, 168 (1900); **36**, 681 (1901); **42**, 68 (1903); **48**, 1 (1904); **51**, 344 (1905); **56**, 195 (1906); **59**, 218 (1907); **60**, 464 (1907); **73**, 641 (1910); **80**, 129 (1912); **86**, 129 (1914); **89**, 1 (1915); **90**, 89, 359 (1915); **91**, 571, 641 (1916); **93**, 154, 570 (1918); Ann. d. Physik (4), **54**, 245 (1917); **61**, 273 (1920); Phil. Mag. (6), **17**, 333 (1909); **20**, 135 (1910); Ann. d. phys. (9), **5**, 78 (1916).

of importance that in the case of a gradient of density of this kind we have to distinguish a *layer of rarefied liquid from a layer of compressed gas*, a two-sidedness of the capillary boundary layer, which makes itself felt in many phenomena.

We may note here a further peculiarity of the surface tension, to which the van der Waals theory of liquids leads directly. At the critical point, liquid and gas become identical, the interface disappears, the interfacial tension becomes zero. How this behaviour of liquids rules throughout the dependence of the surface tension upon temperature cannot be dealt with until later.

It would doubtless be very desirable to start from a general theory of liquids and base the capillary chemistry of liquids upon it. But if we consider how complicated van der Waals' theory of liquids already becomes for a mixture of several substances, we can gauge the difficulty of this task. Nor can we make any direct quantitative use of the progress which has been made of late years from the kinetic point of view in the theory of the structure of crystals and of atoms. We already have, however, a better qualitative understanding of many phenomena, but it would appear advisable to go into further detail in the course of the later discussion.

On account of the great difficulties presented by the theory of the liquid state, I have contented myself with connecting related phenomena of capillary chemistry by a few thermodynamical considerations and the generalization of certain data of experience. This does not mean that molecular-kinetic considerations will not receive attention when they have been successful.[1]

Measurement of Surface Tension

There are few physical quantities for which so many methods of measurement exist as for surface tension at the interface gas—liquid. The cause of this is easily seen : the surface tension is the influence which essentially determines the shape of a liquid in rest and motion ; fundamentally, therefore, we can determine the surface tension from every form of equilibrium of a liquid, and also from every motional form taken by it under the influence of a known external cause. There are, however, a large number of equilibrium forms and also motional forms ; for it is a characteristic of the liquid state that the particles are easily moved relatively to one another.

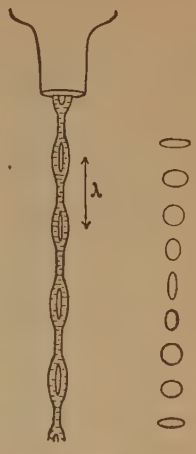
The fundamentally simplest methods of measurement are those in which only the interface liquid—gas comes into question ; where, therefore, no surfaces of solid bodies are present. To these belong

(*a*) The method of vibrating jets.
(*b*) The method of vibrating drops.
(*c*) The method of surface waves.

(*a*) The method of vibrating jets depends upon the following phenomenon. If we allow a liquid to stream out of an opening which is not round, but elliptical or triangular, for example, we do not get a cylindrical

[1] Attention should be drawn to a new theory of liquids by Edser (Fourth Report on the Progress of Colloid Chemistry, B.A., and Research Department, 1922). This theory makes no assumptions regarding the structure of the liquid or of its component molecules, other than that the attraction between the latter is some function (found to be the 8th power) of the distance between them. Relations are found between σ and the internal latent heat, and also the coefficient of thermal expansion. [Trans.]

et, but instead the jet shows periodic enlargements and constrictions (Fig. 3 *a*). In the case of an elliptical opening, for example, we have a succession of lenticular liquid surfaces, in which the planes of any two successive ones are at right-angles to one another.



a *b*

FIG. 3.

After Bidone, Savart, and Magnus had described this phenomenon, Rayleigh [1] showed that it may be explained upon the basis of the surface tension. Piccard,[2] G. Meyer,[3] Watson,[4] and especially Pedersen [5] and Bohr [6] have measured surface tensions according to this method.

This is not the place to develop the theory according to Rayleigh; the following approximate description will suffice. A jet which is not truly circular in section is not a figure of equilibrium. It tends towards a form with a smaller surface; this is first of all the jet of circular section. An oscillation about this position of equilibrium is set up, as we can plainly see from a series of sections which are taken from the jet going from above downwards (Fig. 3 *b*).

If the departure from the circular section is not too great, we may regard the oscillations as isochronous, and may apply the general equation for isochronous oscillations—

$$\frac{\Theta^2}{\pi^2} = \frac{\text{moment of inertia}}{\text{directive force}}$$

where Θ is the period of oscillation. The moment of inertia will be proportional to the mass, and therefore to the density of the oscillating liquid, and will depend in a manner not yet determined upon the shape of the opening. The directive force is a function of the surface tension, and will increase in proportion to it, hence

$$\frac{\Theta^2}{\pi^2} = A\frac{\varrho}{\sigma},$$

where A is a constant, and ϱ and σ are, as always, density and surface tension respectively. If now we consider that

$$\Theta = \frac{1}{n}, \text{ and } n\lambda = v$$

(here n is the frequency, λ the wave-length, and v the velocity of the falling liquid), then

$$\sigma = A\pi^2 \frac{\varrho v^2}{\lambda^2}.$$

With a given velocity of efflux, σ is the greater, the greater the density and the smaller the wave-length.[7]

[1] Proc. Roy. Soc. **29,** 71 (1879) and **34,** 130 (1882). There also the older literature is to be found.

[2] Arch. d. scienc. phys. et nat. (3), **24,** 579 (1890).

[3] Wied. Ann. **66,** 523 (1898). Further *Stocker,* "Die Oberflächenspannung schwingender Flüssigkeitsstrahlen, untersucht an reinem Wasser und wässrigen Salzlösungen." Dissertation, Freiburg i. Br. **1914.**

[4] Phys. Rev. **21,** 59 (1905).

[5] Proc. Roy. Soc. **80,** 26 (1907); Phil. Trans. A. **207,** 341 (1907).

[6] Proc. Roy. Soc. **82,** 146 (1909); **84,** 395 (1911); Phil. Trans. A. **209,** 281 (1909).

[7] This deduction follows that given by *Hagenbach* (*Piccard, loc. cit.* under 2).

The absolute formula deduced by Rayleigh is as follows:

$$\sigma = \frac{4\pi^2 r^3}{\nu^3 - \nu} \frac{\rho v^2}{\lambda^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here r is the radius of the circle of equilibrium, and ν is a number, which depends upon the shape of the opening, being 2 for an elliptical opening, 3 for a triangular, and so on.

Since it is not quite easy to determine r exactly, the method is used for relative measurements with the same efflux orifice. The wave-length λ is determined by photographing the jet and then determining the distance between two loops or nodes; in case of necessity this measurement may be made directly upon the jet by means of a pair of dividers. We must know in addition the density of the liquid and the velocity of efflux. The latter is equal, according to the well-known law of Torricelli, to $\sqrt{2gh}$ where g is the acceleration due to gravity and h the head under which the liquid flows out. If we keep the latter constant, we can dispense with the determination of v.

Pedersen and particularly Bohr carried out absolute measurements. The latter discussed the Rayleigh formula and corrected it by taking into account the effect of viscosity and the inertia of the surrounding air. The reader is referred to these investigations for further work.

This method has been described in detail because, as we shall see later, it has theoretical importance.

(*b*) The method of vibrating drops was used by Lenard[1] and his co-workers. It is similar to the foregoing in many respects. If we allow drops to fall under suitable conditions from a tube, the drop has at the moment of separation from the orifice a form which is not strictly spherical, but, on account of the action of gravity, ellipsoidal. In falling it oscillates about its form of equilibrium, the sphere, and by photographing the drop at different points of its fall, we can determine the period of the oscillation.[2] The formula which leads to the knowledge of the surface tension is derived in a manner quite similar to that for the oscillating jet; it is, omitting certain corrections which are undoubtedly necessary, as follows:

$$\sigma = \frac{3}{8} \frac{w}{\Theta^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where w is the weight of the drop and Θ the period of oscillation.

(*c*) In place of gravity, which hitherto set the liquid in motion, we may naturally employ any other force, say an elastic one. This is the case in

[1] Wied. Ann. **30,** 209 (1887). Heidelb. Akad. 1910, 18 Abh. *Jahnke*, "Best. d, Oberfl. wässrig. Salzlsg. n. d. Methode d. Schwing. fall. Tropfen." Dissertation. Heidelberg, 1909. *Ebeling*, Heidelb. Akad. 1915, 9 Abh.

[2] Instead of photographing the drop, we can also determine the period of oscillation as follows. When it falls into a liquid, each drop is transformed into a vortex ring, and the depth to which the vortex ring penetrates depends upon the phase of oscillation of the drop. It penetrates farthest when the long axis of the ellipse forming the shape of the drop at the extreme of its oscillation stands at right-angles to the liquid surface; it penetrates least far when the long axis is parallel to the liquid surface. The depth of penetration changes therefore periodically in accordance with the phase of oscillation of the drop, and hence according to the height from which it falls: the period of oscillation may be deduced from this [*V. Kutter*, Physik. Zeitschr. **17,** 424, 573 (1916)]. For the same reason the height to which a small drop is thrown back on meeting a completely unwettable, smoked metallic plate also changes periodically with the height of fall, so that the period of oscillation may also be thus determined [*Ollivier*, Ann. de chim. et de phys. (8), **10,** 289 (1907)].

the *method of surface waves*. Here surface waves (ripples) are generated upon a liquid surface, either in the form of linearly advancing or circular standing waves. In the first we allow a glass plate fixed to one limb of an oscillating tuning-fork, in the second case the points of the tuning-fork, to dip 1–2 mm. into the liquid. A microscope directed at the surface from the side allows the wave-length λ to be measured. This is, however, better done by photographing the ripples and then measuring them. If we know the frequency of the tuning-fork n and the density ϱ of the liquid, the surface tension may be calculated from the formula given by W. Thomson[1]:

$$\sigma = \frac{1}{2\pi}\varrho n^2\lambda^3 - \frac{g\lambda^2\varrho}{4\pi^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The second term is a correction term, which takes into account the influence of gravity. For the measurement depends upon the fact that in the case of small liquid waves gravity plays a much smaller part in the tendency to restoration of the plane equilibrium surface than the surface tension, which opposes the increase of surface caused by the rippling.

Faraday and Scott Russell were the first to observe the ripples, Matthiessen[2] was the first to describe them more closely. As already mentioned, W. Thomson developed the theory of the phenomenon; later Rayleigh,[3] Grunmach and others measured surface tensions by this method.

Fig. 4.

All methods in which solid surfaces also occur become less simple on account of the fact that *wetting* has to be taken into account. If we place a drop of any liquid upon the plane surface of a solid body, nothing can be predicted as to its behaviour. There are various possibilities; either the drop remains round, as in the case of mercury upon glass, or it flows away completely and spreads over the plane, as, for example, alcohol upon glass; or neither of these limiting cases occurs—the drop spreads only partially; the interfaces liquid—gas and solid—liquid cut one another at a definite angle (Fig. 4). Such behaviour may be seen in the case of water upon a not particularly clean plate of glass or metal. We have thus the three cases of *non-wetting*, *complete wetting*, and *partial wetting*, with the formation of a *contact angle*; this latter expression denotes the above-mentioned angle between the two interfaces liquid—gas and solid—liquid (α in Fig. 4).

We shall leave till later (p. 157) the question of wetting, and of the

[1] Phil. Mag. (4), **42**, 375 (1871).

[2] Pogg. Ann. **134**, 107 (1868); **141**, 375 (1870); there also will be found other literature.

[3] The following made use of the first method, the oscillating glass plate: *Rayleigh* [Phil. Mag. (5), **30**, 386 (1890)]; *Dorsey* [Phil. Mag. (5), **44**, 369 (1897)]; *Watson* [Phys. Rev. **12**, 257 (1901)]; *Kolowrat-Tscherwinski* [Journ. d. russ. phys.-chem. Ges. **36**, 265 (1904), cited from Beiblätter, **29**, 985 (1905)]. The following used the second method of the vibrating tuning-fork: *Grunmach* [Ann. d. Physik (4), **3**, 659 (1900); **4**, 367 (1901); **6**, 559 (1901); **9**, 1261 (1902); Wissensch. Abh. d. K. Norm. Eich-Komm. **3**, 191 (1902)]; *Kalähne* [Ann. d. Physik (4), **7**, 440 (1902)]; *Brümmer* [Exp. Bestimm. d. Oberfl. wässr. Sulfatlös. Diss. Rostock, 1902]; *Löwenfeld* [Exp. Untersuch. üb. d. Kapillaritätskonst. usw. Diss. Rostock, 1905]. *Pfund* [Phys. Rev. **32**, 324 (1911)] generates the capillary waves by means of the electrostatic action of high-tension alternating current.

existence of a contact angle. The solid boundary surface which most commonly occurs in the measurement of surface tension consists of glass, and in the case of this substance, the limiting values of the contact angle appear to be preferred. In the case of liquids like water, aqueous solutions, organic liquids, and so forth, we have a zero contact angle, or complete wetting ; in the case of mercury, molten metals, and some other materials, one of 180°, or non-wetting. There is much, however, that tells in favour of the appearance of definite contact angles at other boundary surfaces. This is especially true of water and aqueous solutions upon solid metals and upon other substances, inorganic and organic. In the following discussion it will be assumed that the glass used is well cleaned, and hence completely wettable.

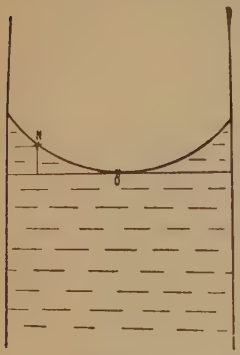


Fig. 5.

In contrast to the methods already described, those which now follow are chiefly concerned with the equilibrium form of the liquid as it results from the interaction between gravity and surface tension. Laplace has already deduced the general differential equation for a liquid which is contained in a vessel of any shape. If the surface of the liquid has a curvature of any form, determined by gravity and the surface tension (Fig. 5), there is a pressure K at the lowest point O of the surface according to equation (5) on p. 9. If we take into account that the surface is concave, and that σ is put equal to $\frac{H}{2}$, we have at a point N, lying at a point in the curved surface z cm. higher than O, on the one hand the pressure

$$K - \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

and on the other the weight of a column of liquid 1 sq. cm. in area and of height z above the plane passing through O, that is to say, a weight of $z\varrho g$ grams, where ϱ and g are the density of the liquid and the acceleration due to gravity respectively. In equilibrium the hydrostatic pressure of a liquid is everywhere the same, hence

$$z\varrho g - \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If we express the radii of curvature at the points O and N in known manner as functions of the co-ordinates passing through O, we recognize that we have the differential equation which describes generally the curvature of a surface under the influence of gravity and of surface tension. Whether and how accurately it can be integrated depends upon the peculiarities of the experimental arrangement.

The number of methods of measurement is in part doubled through the fact that we can use either the behaviour of a drop of liquid in a gas space or of a gas bubble in a space filled with liquid. We can thus distinguish the following methods :

(*d*) The surface tension is determined by direct measurement of the curvature of a liquid surface.
(*e*) The method of flat drops and bubbles.
(*f*) The capillary rise method.

(*g*) The method of adhesion plates and rings.

(*h*) The determination of drop-weight or gas-bubble pressure.

(*d*) The *method of curvature measurement* depends upon the determination of the curvature of a suitable surface in a state of equilibrium, and the calculation of the surface tension from this and other dimensional magnitudes of the surface. We generate, for example, a meniscus of liquid of known diameter, and allow an object of known size to produce its mirror image in the liquid surface. From the size of the object and of its image, which is measured by a microscope, and the distance between the two, we get the radius of curvature of the surface. As we see, contact with solid surfaces only takes place at the sharp walls of the end of the tube ; wetting does not therefore come seriously into question, and the method is therefore fundamentally one in which we are only dealing with the interface liquid —gas.

It was, however, used by König [1] at Helmholtz' suggestion for the measurement of the tension mercury-aqueous solution ; G. Meyer [2] worked with it for the same purpose ; Stöckle [3] used it for the determination of the tension between mercury and gases ; the methods of Eötvös,[4] Raman,[5] Anderson and Bowen,[6] and others are similar.

The calculation of the surface tension from the data found by this method is frequently inconvenient. It is true that Poisson [7] integrated the differential equation (4) mentioned on p. 16 by neglecting certain quantities ; but for the dimensions which can be used experimentally the formula thus obtained is not, as Lohnstein [8] showed, exact enough, even when we apply further corrections, as König and others did. According to the procedure of Lohnstein, Stöckle, and others, it is therefore advisable to have recourse to the tables of Bashforth and Adams.[9] In these, the surface tensions got by mechanical quadrature are tabulated against the characteristic dimensions of the meniscus (diameter, relation of the radii of curvature in the centre to the co-ordinates of the meniscus).

(*e*) The method worked out by Quincke [10] of the large *flat liquid drop* resting upon a plane surface, or of a similar *gas-bubble* in a liquid beneath a plane solid surface, hardly differs in essentials from the preceding method ; but here we can, by choosing suitable dimensions, simplify the calculation to such an extent that we get a formula which enables σ to be calculated from the characteristic measurable dimensions of the drop or bubble. The simple formula deduced by Quincke was not, it is true, sufficiently accurate ; it is necessary to use the more complicated expressions which have been given by Worthington [11] and particularly Lohnstein.[12]

This method has also been used to determine σ for metals, and the measurements were carried out after the metallic drops had solidified. Gradenwitz [13] showed, however, that the contraction upon solidification causes changes of form, which produce great uncertainty in the results of these experiments.

[1] Wied. Ann. **16,** 1 (1882).
[2] Wied. Ann. **53,** 864 (1894).
[3] Wied. Ann. **66,** 499 (1898).
[4] Wied. Ann. **27,** 448 (1886).
[5] Phil. Mag. (6), **14,** 591 (1907).
[6] Phil. Mag. (6), **31,** 143 (1915).
[7] "Nouvelle théorie de l'action capillaire," p. 216.
[8] Wied. Ann. **54,** 713 (1895).
[9] "An Attempt to test the Theories of Capillary Action." Cambridge, 1883.
[10] Pogg. Ann. **139,** 1 (1870).
[11] Phil. Mag. (5), **20,** 51 (1885).
[12] Wied. Ann **53,** 1062 (1894).
[13] Wied. Ann. **67,** 467 (1899).

(*f*) The method used most frequently is that of the *capillary rise*. It depends upon the fact, already frequently referred to, that liquids take up a different vertical height in capillary spaces, in capillary tubes or between plates which are very close together, from that in wide vessels. Wetting is here of decisive importance inasmuch as non-wetting liquids such as mercury take up a lower position in capillary spaces, and wetting liquids a higher one, than in wide vessels.

In order to deduce the relation between the height of rise and the surface tension, it is not necessary to start from the differential equation given above, although it can be integrated sufficiently accurately for this limiting case. Simple considerations give us the required result.

Let a capillary tube ABCD (Fig. 6) dip into a liquid which wets it. The liquid will cover all solid surfaces with a film of liquid. In the interior of the tube, therefore, the surface ABEF would be covered with liquid. The surface tension strives to reduce as much as possible this large surface which is in contact with the gas-space. Consequently, the liquid rises in the tube, so that only the smaller surface ABGH is now covered with liquid. Equilibrium is present when the force of the surface tension acting upwards balances the weight of the column of liquid which has been raised.

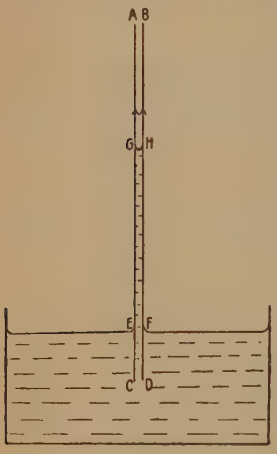


FIG. 6.

The surface tension acts around the periphery of the tube section ; since σ is the tension per unit of length, the force acting upwards has the value $2\pi r\sigma$, where r is the radius of the tube. The weight of the column of liquid is, in absolute units, and without taking the buoyancy of the air into account, $\pi r^2 h\varrho g$, where h is the capillary rise, ϱ the density of the liquid, and g the acceleration due to gravity. In equilibrium therefore we have

$$2\pi r\sigma = \pi r^2 h\varrho g \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

hence

$$\sigma = \tfrac{1}{2} r h\varrho g \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In the case of a non-wetting liquid the argument is quite similar ; the surface, which corresponds to CDEF, is now covered with a layer of gas. The surface tension acts downwards and produces the effect that the liquid offers a smaller convex surface to the gas. Here also the surface tension supports the column of liquid forced out of the tube, so that the above formula is valid.

In the same way, the equation for the case of two parallel plates may be deduced. It runs

$$\sigma = \tfrac{1}{2} a h\varrho g,$$

where a is the distance between the plates. As we see, a liquid rises between two plates to the same height as in a capillary tube of radius equal to the distance between the plates. Grunmach [1] has further worked out the case, in which a liquid rises between two plates placed at an angle to one another and enclosing a wedge-shaped space.

[1] Physik. Zeitschr. **11**, 980 (1910).

In the capillary rise method, the height of the liquid in a capillary tube has to be compared with that in a wide tube, which may be done with the help of a scale or cathetometer. Further, the radius of the tube must be determined for the point, be it noted, at which the capillary meniscus stands, since the pressure of the liquid is communicated equally in all directions. We have also to know the density of the liquid.

The method has been used by a large number of investigators. Volkmann [1] especially has discussed in detail all sources of error. Very careful measurements have been made by Th. W. Richards and Coombs.[2]

For relative measurements it is convenient to have the capillary tube, of about 0·25 mm. diameter, sealed on to a wider tube so as to form a U-tube. This measuring tube is fixed by clamps upon a scale drawn on mirror glass, which can be hung up vertically upon a stand. It is important in measuring the capillary rise to wash out the capillary carefully with strong nitric acid or a mixture of chromic and sulphuric acids, and never to use it dry, but always to keep it under water.[3]

The measurement of the level of the liquid in the wider vessel is comparatively inaccurate in such determinations. For relative measurements it is therefore useful, according to L. Michaelis,[4] to use two capillary tubes of different width firmly fixed together and dipping into the liquid, and to read the difference in level of the liquid in the two tubes. This is, as is easily seen, proportional to the surface tension.

In deducing the capillary rise formula the assumption introduced on p. 16 was made that in the case of a wetting liquid the angle of contact is zero ; only in this case does the surface tension pull vertically upwards, in the direction of the arrow in Fig. 6. If we do not make this assumption, we may get the general equation for the case in which a liquid in a capillary tube communicates with a liquid having a plane surface, as follows.

Let the Laplace equation (p. 16) be applied to the case in which the point O lies upon the plane surface of the liquid, while the point N lies in the meniscus in the capillary tube. Then since R_1 and R_2 are infinite for a plane surface, the second term of the equation disappears. There remains, if we substitute for z the height h of N above O,

$$\sigma\left(\frac{1}{R_1}+\frac{1}{R_2}\right)=h\varrho g.$$

If the capillary tube is sufficiently narrow, and r less than 1 mm., we may take the meniscus surface as spherical with the radius R, and get the equation

$$\sigma=\tfrac{1}{2}Rh\varrho g.$$

We have now therefore to determine in place of the radius of the tube the radius of curvature of the meniscus surface in the capillary tube. This method was employed by Magie,[5] who measured this curvature as described on p. 17. Since his results agree entirely with those obtained by the simple rise method, we might take this as a proof that the angle of contact

[1] Wied. Ann. **11,** 177 (1880); **17,** 353 (1882); **28,** 135 (1886); **53,** 633 and 664 (1894); **56,** 457 (1895); **62,** 507 (1897); **66,** 194 (1898).

[2] Journ. Am. Chem. Soc. **37,** 1656 (1915); see also *Harkins* and *F. E. Brown, ibid.* **41,** 499 (1919).

[3] *Drucker,* Zeitschr. f. physik. Chemie, **52,** 641 (1905).

[4] *L. Michaelis,* Praktik d. physikal. Chemie, 61 (1921).

[5] Wied. Ann. **25,** 421 (1885).

of wetting liquids is strictly zero ; but it is questionable whether the method is sufficiently delicate.

As we see, the equation

$$\sigma = \tfrac{1}{2}\mathrm{R}h\varrho g$$

becomes identical with the equation

$$\sigma = \tfrac{1}{2}rh\varrho g,$$

when the radius of curvature R is equal to the radius r of the tube. This is the case when the surface of the meniscus is a hemisphere, or when the edge of the meniscus meets the wall of the tube at an angle 0°.[1]

On the basis of these measurements of capillary rise, it may be shown that $\sigma = \frac{\mathrm{H}}{2}$ (see p. 9). If we had not replaced $\frac{\mathrm{H}}{2}$ by σ in equation (4) on p. 16, we should have obtained in the case considered an equation

$$\frac{\mathrm{H}}{2}\left(\frac{1}{\mathrm{R}_1} + \frac{1}{\mathrm{R}_2}\right) = h\varrho g.$$

If we assume a spherical meniscus surface and hence complete wetting, then the left-hand side of this equation becomes equal to $\frac{\mathrm{H}}{r}$, hence

$$\frac{\mathrm{H}}{r} = h\varrho g.$$

Since according to equation (5) on p. 18.

$$2\pi r\sigma = \pi r^2 h\varrho g,$$

we get, when we substitute for $h\varrho g$ the expression $\frac{\mathrm{H}}{r}$, $\sigma = \frac{\mathrm{H}}{2}$.

(*g*) *The method of adhesion of plates and rings* can only be used in the case of wetting liquids. We proceed as follows. A plate or ring of suitable material (glass or platinum), which hangs exactly horizontal from one end of a balance beam, is dipped into the liquid. If we now load the other side of the balance with weights, the plate or ring is raised out of the liquid, and a column or rather lamella of liquid remains hanging upon it. The weight is now carefully increased either until the column or the lamella tears (among later workers Timberg,[2] Weinberg,[3] and others), or only until the plane of the raised liquid stands at right-angles to the plate (Gallenkamp [4]) which may be determined by a reflection method. The method is fundamentally of the same kind as that used to deduce the concept of surface tension on p. 6.

As regards the calculation, the weight upon one side of the balance equals the pull of the surface tension downwards plus the weight of the column of liquid raised. The different limiting cases lead to equations, for

[1] Particular varieties of the capillary rise method were used by *Sentis* [Journ. de phys. (2), **6**, 571 (1887), (3) **6**, 183 (1897)] and *Gradenwitz* [Neue Methode z. Bestimm. v. Kapillarkonst. verdünnt. Lös. Diss. Breslau, 1902]. *Verschaffelt* and *van der Noot* [Bull. Acad. Roy. Belg. 1911, p. 383] discuss in detail how the influence exerted by the form of the meniscus may be strictly taken into account. *Kiplinger* [Journ. Am. Chem. Soc. **42**, 472 (1920)] describes an arrangement in which only one or two drops of the liquid are required for a measurement.

[2] Wied. Ann. **30**, 545 (1887).

[3] Zeitschr. f. physik. Chemie, **10**, 34 (1892); see also a criticism by *Lohnstein*—Zeitschr. f. physik. Chemie, **10**, 504 (1892).

[4] Ann. d. Physik (4), **9**, 475 (1902) ; see also *Lohnstein* [Ann. d. Physik (4), **25**, 807 (1908)].

which the reader is referred to the papers of the various investigators.[1]

This method is to be particularly recommended, for determining the σ of any plane liquid surface which it is desired to disturb as little as possible.

(*h*) Absolute measurements cannot easily be carried out by the *method of drop-weight and bubble-pressure*; but they are suitable for quick, relative measurements. The law called after Tate,[2] that the weight w of a drop which has formed slowly at the end of a tube and fallen off, is proportional to the surface tension and the periphery of the tube section $2\pi r$, that is

$$w = 2\pi r\sigma k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

does not agree with the theory of capillarity; on the contrary, the detailed investigations of Lohnstein[3] lead to a relation

$$w = 2\pi r\sigma f\left(\frac{r}{a}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Here a is equal to $\sqrt{\frac{2\sigma}{\varrho}}$, where ϱ as usual denotes the density; Lohnstein gives a table for $f\left(\frac{r}{a}\right)$. He discusses and calculates according to this formula a number of measurements of earlier observers (I. Traube,[4] Rayleigh,[5] Guye and Perrot[6]) and finds satisfactory agreement with theory. That Tate's law in many cases is very approximately true arises from the fact, as Lohnstein shows, that in the range of values of $\frac{r}{a}$ which mostly appear in the practical experiments, $f\left(\frac{r}{a}\right)$ is sensibly constant, and has a value of about 0·62.

Livingstone Morgan and his co-workers[7] have elaborated the drop-weight method in detail for relative measurements. They assume strict proportionality between drop-weight and surface tension. According to what has been said above, this is not fully justified; but they chose the diameter of the tube in their experiments such that the departures from Tate's law were comparatively negligible, and accordingly assumed the proportionality constant according to theory.[8]

Another method suitable for relative measurement is the determin-

[1] A closely allied method depends upon the determination of the weight of liquid which hangs upon a plate dipping vertically into the liquid. [*Hall*, Phil. Mag. (5), **36,** 385 (1893); *Foley*, Phys. Rev. **3,** 381 (1896); *Knipp*, Phys. Rev. **11,** 129 (1900)].

[2] Phil. Mag. (4), **27,** 176 (1864).

[3] Ann. d. Physik (4), **20,** 237 and 606 (1906); **21,** 1030 (1906); **22,** 737 (1907); Zeitschr. f. physik. Chemie, **64,** 686 (1908); **84,** 410 (1913); further also *Kohlrausch* [Ann. d. Physik (4), **20,** 798 (1906); **22,** 191 (1907)].

[4] Journ. für prakt. Chemie, **34,** 292 and 515 (1886).

[5] Phil. Mag. (5), **48,** 321 (1899). Here *Rayleigh* already develops by a somewhat different method from that of *Lohnstein* a more exact formula for the dependence of the drop-weight upon the surface tension.

[6] Arch. scienc. phys. et nat. (4), **11,** 225 (1901); **15,** 132 (1903).

[7] *Morgan* and *R. Stevenson*, Zeitschr. f. physik. Chemie, **63,** 151 (1908); *Morgan* and *Higgins*, *ibid.* **64,** 170 (1908); *Morgan*, *ibid.* **77,** 339 (1911); *Morgan*, *ibid.* **78,** 129 (1912); *Morgan* and *Cann*, Journ. Am. Chem. Soc. **33,** 1060 (1911).

[8] See *Lohnstein*, Zeitschr. f. physik. Chemie, **64,** 686 (1908); **84,** 410 (1913); on the other hand *Morgan*, Zeitschr. f. physik. Chemie, **89,** 385 (1915); further also *Cénac*, Ann. de chim. et de phys. (8), **29,** 298 (1913); *Harkins* and *Humphery*, Journ. Am. Chem. Soc. **38,** 228 (1916); *Harkins* and *F. E. Brown*, *ibid.* **38,** 246 (1916).

ation of the drop-weight by means of the *stalagmometer* introduced by I. Traube.[1] The number of drops is determined which are formed at a slow rate of flow from a volume of liquid contained in the vessel A (Fig. 7) between two marks *a* and *b*. In order that the drops may be formed sufficiently slowly, a piece of capillary tube K is inserted before the efflux orifice. The latter ends in a ground surface, which ensures that the point of separation of the drop is accurately defined, whereas in the case of formation upon the end of a tube, the liquid wets the outside walls and breaks off them irregularly. The drops must form sufficiently slowly, as otherwise their size would depend not only upon surface tension and gravity, but also upon the kinetic energy of the outflowing liquid. Knowing the volume and density of the liquid contained in the vessel A, and the number of drops, we are able to calculate the drop-weight, put this proportional to the surface tension, and thus, by making relative determinations with a liquid of known surface tension, find the surface tension of an unknown liquid. The method is suitable for rapid working and hence has been widely adopted.

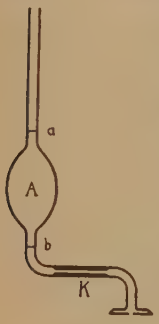


Fig. 7.

As regards the method of bubble pressure, Cantor [2] has worked out the theory for the absolute determination of σ. Feustel,[3] Magini,[4] and particularly F. M. Jaeger [5] have carried out a large number of measurements by the method. Here also the great majority of the observers, G. Jäger,[6] Hock,[7] Linebarger,[8] Whatmough,[9] have been satisfied with relative measurements. The arrangement recommended by Czapek [10] is very convenient, allows of rapid measurement, and requires only small quantities of liquid.

In the case of absolute measurements, a capillary tube with its edge ground as sharp as possible dips into the liquid to be investigated. Air, or a suitable indifferent gas such as nitrogen, is now forced into the capillary tube, so that bubbles escape at the end of the tube, and the maximum pressure is then determined which can be reached with a slow escape of bubbles. If p is this maximum pressure, r the radius of the capillary, ϱ the density of the liquid, then

$$\sigma = \frac{r}{2}p\left\{1 - \frac{2}{3}\frac{\varrho r}{p} - \frac{1}{6}\frac{\varrho^2 r^2}{p^2}\right\}. \quad . \quad . \quad . \quad . \quad . \quad (9).$$ [11]

[1] Ber. d. deutsch chem. Ges. **20,** 2644 (1887). See also *Abderhalden,* Handbuch der biochem. Arbeitsmethoden, 1912, and *Traube* and *Somogyi,* Internat. Zeitschr. phys.-chem. Biologie, **1,** 485 (1914).

[2] Wied. Ann. **47,** 399 (1892).

[3] Ann. d. Physik (4), **16,** 61 (1905).

[4] Atti R. Accad. dei Lincei, **19,** II. 184 (1910); **20,** I. 30 (1911).

[5] Koninkl. Akad. v. Wetensch. Amsterdam, **17,** 329, 365, 386, 395, 405, 416, 555, 571 (1914); Zeitschr. f. anorgan. und allgem. Chemie, **101,** 1 (1917).

[6] Wien. Akad. d. Wissensch. **100,** II*a*, 245 and 493 (1891).

[7] Wien. Akad. d. Wissensch. **108,** II*a*, 516 (1899).

[8] Amer. Journ. of Science. **18,** 514 (1896).

[9] Zeitschr. f. physik. Chemie, **39,** 129 (1902).

[10] "Über eine Methode z. direkt. Bestimmung d. Oberfl. d. Plasmahaut v. Pflanzenzellen." Jena, G. Fischer, 1911.

[11] This is the correct form of the equation according to *Schrödinger* [Ann. d. Physik (4), **46,** 413 (1915)]: as regards the theory of the formula see also *F. M. Jaeger* [Koninkl. Akad. v. Wetensch. Amsterdam, **1,** 521 *et seq.* (1914)] and *Ferguson* [Phil. Mag. (6), **28,** 128 (1914)].

If a sharp-edged tube is used, the contact-angle is eliminated just as in the similar cases of the measurement of curvature and of drop-weight determinations.

TABLE 1

Surface Tension of Water at 18°

Method.	σ.	Observer.
Vibrating jets	73	Rayleigh [1]
,, ,,	73·8	Pedersen [2]
,, ,,	72·4	Bohr [3]
,, ,,	72·5	G. Meyer [4]
Vibrating drops	73	Lenard [5]
Capillary waves	74·0	Rayleigh [6]
,, ,,	73·3	Dorsey [7]
,, ,,	76	Grunmach [8]
,, ,,	72·3	Kolowrat-Tscherwinski [9]
,, ,,	73·8	Kalähne [10]
,, ,,	75·7	Löwenfeld [11]
Curved surfaces	73·5	Lohnstein [12]
Flat air-bubbles	73	Quincke [13] (calc. Worthington) [14]
Capillary rise	73·1	Volkmann [15]
,, ,,	73·0	Domke [16]
,, ,,	72·7	Worley [17]
,, ,,	73·1	Harkins and F. E. Brown [18]
Adhesion ring of platinum	76·8	Timberg [19]
,, ,, copper	76·8	Weinberg [20]
Adhesion plate	73·1	Hall [21]
Drop-weight	73·8	Ollivier [22] (calc. Lohnstein) [23]
Bubble-pressure	75·2	Cantor [24]
,, ,,	76·3	Forch [25]
,, ,,	73·7	Magini [26]
,, ,,	72·7	F. M. Jaeger [27]

The Agreement of the various Methods

The large number of methods of measurements allow us to test the question as to how definitely the surface tension can be measured. In Table I a considerable number of measurements of the surface tension of water at 18° are given, partly following a compilation of Kalähne.[28]

The greater part of the values lie around 73. Some are considerably greater, up to 75 and even 76. We might at first think that the water investigated had not been of sufficient purity; and since, as we shall see

[1] Proc. Roy. Soc. **29,** 71 (1879) and *Worthington* [Phil. Mag. (5), **20,** 51 (1885)].
[2] *loc. cit.* p. 13. [3] *loc. cit.* p. 13. [4] *loc. cit.* p. 13.
[5] *loc. cit.* p. 15. [6] *loc. cit.* p. 15. [7] *loc. cit.* p. 14.
[8] *loc. cit.* p. 15. [9] *loc. cit.* p. 15. [10] *loc. cit.* p. 15.
[11] *loc. cit.* p. 15. [12] Wied. Ann. **53,** 1062 (1894).
[13] *loc. cit.* p. 17. [14] See under reference.[1]
[15] Wied. Ann. **66,** 164 (1898).
[16] Wiss. Abh. d. K. Norm. Eich-Komm. **3,** 38 (1902).
[17] Journ. Chem. Soc. **105,** 266 (1914).
[18] Journ. Amer. Chem. Soc. **41,** 499 (1919).
[19] *loc. cit.* p. 20. [20] *loc. cit.* p. 20. [21] *loc. cit.* p. 21.
[22] Ann. d. chim. et d. phys. (8), **10,** 245 (1907).
[23] Zeitschr. f. physik. Chemie, **64,** 689 (1908).
[24] *loc. cit.* p. 22. [25] Ann. d. Physik (4), **17,** 744 (1905).
[26] *loc. cit.* p. 22.
[27] Zeitschr. f. anorgan. u. allgem. Chemie, **101,** 56 (1917). [28] *loc. cit.* p. 15.

later, quite small impurities suffice to lower the surface tension of water very considerably, we are tempted to ascribe especial weight to the higher values.

But another source of error appears to claim still closer attention. The question must be carefully investigated whether the formula which is used for the calculation of the surface tension really corresponds sufficiently well to the experimental conditions, or whether terms of importance have been neglected. Thus Bohr [1] drew attention to the fact that in the method of capillary waves, the following source of error has not been sufficiently taken into account. The formula used for calculation (see p. 15) refers to sufficiently large distances from the wave generator (points of tuning-fork, vibrating plate), as may be seen in the deduction of the formula. This condition was probably not fulfilled in the case of the measurements which gave values for the surface tension which were too high. In the case of the experiments of Kolowrat-Tcherwinski, and probably also those of Dorsey and Kalähne, it was fulfilled, and the surface tension had a lower value. This is therefore to be regarded as the more correct.

In the case of the method of bubble-pressure, which also gives too high values, a similar error probably occurs. Later measurements, which were carried out with a glass capillary by Magini and F. M. Jaeger, gave much lower values than the older measurements carried out with a platinum capillary by Cantor and Forch. Magini compared platinum capillaries with glass capillaries, and arrives at the conclusion that glass capillaries are more trustworthy than platinum capillaries, since the edge is sharper and smoother, and the form of the section is more perfectly circular. The smaller values are therefore to be preferred.

Hence it is probable that the higher values of Timberg and Weinberg are also affected by some physical source of error.[2]

On account of the above considerations, we shall assume in the following pages the value 73 dyne/cm. as the most probable for the surface tension of water at 18°; at 20° therefore a value 72·8. As temperature coefficient for water and dilute aqueous solutions a value of $\gamma = 0{\cdot}002$ was used for recalculations (see p. 28). It is not impossible, however, that the true value of the surface tension of water lies somewhat lower, perhaps at about 72·5 for 18°, as the experiments of Bohr and others have given.

In general, it is at the present time difficult to be sure of a surface tension to nearer than 1–2 per cent., although a single method may yield values in closer agreement with one another.

When we speak in the following pages of the surface tension of pure substances, the "ideal" surface tension at the interface liquid vapour is meant. Since this is not known in many cases, the surface tension against air or against an indifferent gas is used in place of it, the assumption being made that the two values differ very little from one another. This is, as we shall see later (p. 84), entirely permissible. It may be said in advance that, of the measurements of σ here mentioned, those of Schiff, Eötvös, Ramsay and Shields, and of Knipp refer to the interface liquid—vapour.

The Surface Tension of Pure Liquids

The surface tension of a large number of pure liquids has been measured. The values vary from $\frac{1}{10}$ to some 1,000 dyne/cm. We easily get a general

[1] Phil. Trans. **209**, A, 316–317 (1909).

[2] A source of error which should probably be taken particular account of is, that the angle at which the liquid lamella tears off is not accurately known, and that we are probably not dealing with a case of complete wetting, but one in which a contact-angle comes into the calculation.

view when we remember that the surface tension must become zero at the critical point. Hence liquids which are known to us only in a state very near to this point, for example the liquefied gases, have a very small surface tension, and those which are very far from their critical point, such as the molten metals, a very high one.

A number of the methods described can be used under extreme conditions. For measurements at high temperatures (molten metals, salts, and such-like) it is advisable to use the method of drop curvature (Quincke,[1] Siedentopf [2]) and particularly of bubble-pressure (F. M. Jaeger [3]; the gas which came into contact with the liquid was dry nitrogen); convenient, if somewhat untrustworthy, is the determination of drop-weight, by means of which Quincke [4] measured the surface tension of many molten substances. Baly and Donnan,[5] also Verschaffelt,[6] used the capillary-rise method at low temperatures; while Grunmach [7] used the capillary-rise method for molten metals as well as for liquefied gases.

The following tables give a general view of the σ values for the most important substances; they are not all very accurately known, but the order of magnitude is undoubtedly correct.

TABLE 2

Surface Tension of Liquefied Gases, the Halogens, etc.

Substance.	Temp. in °C.	σ.	Observer.
Hydrogen	− 252	2	Dewar [8]
Nitrogen	− 195·9	8·3	Grunmach,[9] Baly and Donnan [10]
Oxygen	− 182·7	13	,, ,,
Argon	− 186·1	12·7	Baly and Donnan [10]
Fluorine	− 187	14	Moissan and Dewar [11]
Chlorine	− 72	33·6	Grunmach [12]
Bromine	+ 20	38·0	Ramsay and Aston [13]
Phosphorus	+ 78·3	43·1	,, ,,
Hydrogen peroxide	+ 9·6	34·7	Spring [14]
Carbon monoxide	− 190	11	Baly and Donnan [10]
Carbon dioxide	+ 15·2	1·8	Verschaffelt [15]
Ammonia	− 29	41·8	Grunmach [12]
Nitrous oxide	− 89·3	26	Grunmach [16]
Sulphur dioxide	− 25	33·5	Grunmach [12]
Sulphur trioxide	+ 20	30	Schenck [17]

[1] Pogg. Ann. **138,** 141 (1869). Note also the objections of *Gradenwitz, loc. cit.* .p. 17.
[2] Wied. Ann. **61,** 235 (1897).
[3] *loc. cit.* p. 22. Measurements over range − 80° to + 1650°.
[4] Pogg. Ann. **135,** 62 (1868).
[5] Journ. Chem. Soc. **81,** 907 (1902). For the correct calculation of the values incorrectly given for argon see *Rudorf* [Ann. d. Physik (4), **29,** 764 (1909). Phil. Mag. (6), **39,** 238 (1920)].
[6] Kon. Akad. v. Wetensch. **4,** 74 and 94 (1895–96); cited from Beiblätter, **20,** 343 (1896) and **21,** 16 (1897).
[7] Ann. d. Physik (4), **3,** 660 (1900); **4,** 367 (1901); **22,** 107 (1907).
[8] Proc. Roy. Soc. **68,** 360 (1901).
[9] Ann. d. Physik (4), **22,** 107 (1907).
[10] *loc. cit.*, under 5.
[11] Compt. rend. **125,** 505 (1897).
[12] Ann. d. Physik (4), **4,** 367 (1901).
[13] Journ. Chem. Soc. **65,** 173 (1894).
[14] Zeitschr. anorg. Chemie, **8,** 424 (1895).
[15] Kon. Akad. v. Wetensch. **4,** 74 (1895–96); cited from Beibl. **20, 343** (1896).
[16] Ann. d. Physik (4), **15,** 401 (1904).
[17] Lieb. Ann. **316,** 1 (1901).

TABLE 3

Surface Tension of Metals

Substance.	Temp. in °C.	σ.	Observer.
Sodium (against CO_2)	90	520	Quincke [1]
Potassium „	58	360	„
Copper „	1,080	about 1000	R. Herzfeld [2]
Silver	1,060	750	Gradenwitz [3]
Gold	1,070	612	Heydweiller [4]
Cadmium	365	810	Siedentopf [5]
Mercury (in vacuo)	15	436	Stöckle [6]
Tin	277	610	Siedentopf [5]
Lead	389	500	„
Antimony (against CO_2)	432	240	Quincke [7]
Bismuth	346	420	Siedentopf [5]
Iron	1,200	about 1000	Quincke [7]
Platinum	1,770	about 1500 —2000	„

TABLE 4

Surface Tension of Molten Salts

Substance.	t in degrees.	σ.	Observer.
LiCl	608	140	F. M. Jaeger [8]
NaF	990	202	„
NaCl	801	114	„
NaBr	768	106·5	„
NaJ	660	88·2	„
$NaNO_3$	312	121	„
Na_2SO_4	884	196	„
Na_2CO_3	850	213	I. Traube [9]
KF	858	143	F. M. Jaeger [8]
KBr	734	88·8	„
KJ	681	78·3	„
KCNS	160	110	Bottomley [10]
KNO_3	339	113	F. M. Jaeger [8]
K_2SO_4	1,074	144·5	„
K_2CO_3	880	170	I. Traube [9]
RbCl	720	98·3	F. M. Jaeger [8]
CsCl	646	91·3	„
$CaCl_2$	780	160	Motylewski [11]
$SrCl_2$	850	170	„
$BaCl_2$	960	180	„

[1] Pogg. Ann. **135,** 621 (1868).
[2] Wied. Ann. **62,** 450 (1897); but see [3].
[3] Wied. Ann. **67,** 467 (1899).
[4] Wied. Ann. **62,** 694 (1897).
[5] Wied. Ann. **61,** 235 (1897); *Grunmach* [Ann. d. Physik (4), **3,** 660 (1900)] finds the much smaller value for tin of about 350.
[6] Wied. Ann. **66,** 499 (1898).
[7] Pogg. Ann. **135,** 621 (1868).
[8] Zeitschr. anorg. u. allg. Chemie, **101,** 1 (1917).
[9] Ber. d. deutsch. chem. Ges. **24,** 3074 (1891).
[10] Journ. Chem. Soc. **83,** 1421 (1903).
[11] Zeitschr. anorg. Chemie, **38,** 410 (1903); there will be found a large number of measurements of salts of heavy metals and of polybasic acids.

TABLE 5

Surface Tension of Organic Compounds

Substance.	Temp. in °C.	σ.	Observer.
Hexane	20	17·4	Dutoit and Friderich [1]
Paraffin	54	30	Quincke [2]
Benzene	20	28·8	Volkmann [3]
Toluene	20	28·2	,,
Methyl alcohol	20	23·0	Ramsay and Shields [4]
Ethyl alcohol	20	22·0	,, ,,
n-Propyl alcohol	20	28·6	,, ,,
Isobutyl alcohol	20	22·5	,, ,,
Isoamyl alcohol	20	23·5	,, ,,
Ethyl ether	20	16·5	,,
Glycol	20	46·1	,, ,,
Glycerine	18	64·5	Domke [5]
Acetone	20	22·6	F. M. Jaeger and Smit [6]
Formic acid	20	37·1	Ramsay and Shields [4]
Acetic acid	20	23·5	,, ,,
Propionic acid	20	26·2	,, ,,
n-Butyric acid	20	26·3	,, ,,
Aniline	20	43·8	Volkmann [3]
Pyridine	20	38·0	Ramsay and Shields [4]
Nitrobenzene	20	41·8	,, ,,
Chloroform	20	26·3	F. M. Jaeger and Smit [6]
Carbon tetrachloride	20	25·7	Ramsay and Shields [4]
Carbon disulphide	20	33·5	,, ,,

THE DEPENDENCE OF THE SURFACE TENSION UPON TEMPERATURE AND CHEMICAL COMPOSITION

Since, as has already been said, the surface tension becomes zero at the critical point, it is to be expected that it will decrease with rise of temperature. This is very largely the case (but see p. 76). The alteration of

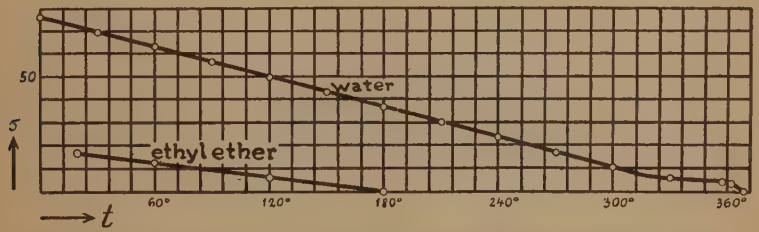


FIG. 8.—σ, t Curves of Water (Knipp[7]) and Ethyl Ether (Ramsay and Shields[8]).

[1] Arch. d. scienc. phys. et. nat. (4), **9**, 105 (1900).
[2] Pogg. Ann. **138**, 141 (1869).
[3] Wied. Ann. **56**, 457 (1895).
[4] Zeitschr. physik. Chemie, **12**, 433 (1893).
[5] *loc. cit.* p. 23.
[6] Koninkl. Akad. v. Wetensch. Amsterdam, **17**, 370 (1914).
[7] *loc cit.* p. 21.
[8] *loc. cit.*, under 4.

σ with temperature is not great; it can be represented over moderate ranges by a linear equation of the form

$$\sigma_t = \sigma_0[1 - \gamma(t - t_0)] \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(see Fig. 8). For σ_0 we may conveniently take the surface tension at the melting-point t_0.[1]

The value of γ may be approximately calculated from the fact that at the critical temperature θ_0 the surface tension is zero. It therefore follows from the above equation that

$$\gamma = \frac{1}{\theta_0 - t_0}.$$

How far the observed values of γ agree with the calculated values is shown by the following Table 6. In it the values of θ_0 and t_0 are taken from the tables of Landolt-Börnstein-Roth, while under "Observer" the investigators are given to whom the values of σ_0 and γ are due.

TABLE 6

Temperature Coefficient of Surface Tension and Critical Temperature

Substance.	σ_0.	θ_0.	t_0.	$\theta_0 - t_0$.	γ obs.	γ calc.	Observer.
Nitrogen	12·1	−146	−210·5	64·5	0·018	0·016	Baly and Donnan [2]
Argon	11·7	−117·4	−187·9	70·5	0·013	0·014	" "
Carbon monoxide .	13·5	−139·5	−207	67·5	0·013	0·015	" "
Water	75·7	+374	0	374	0·0020	0·0027	Volkmann [3], Forch [4]
Ethyl alcohol . .	27·0	+243·1	−117·6	360·7	0·0022	0·0028	Magini [5]
Acetic acid . . .	28·9	+321·6	+ 17·5	304·1	0·0038	0·0033	Feustel [6]
Benzene	29·4	+288·5	+ 5·6	282·9	0·0035	0·0035	Renard and Guye [7]
Phenol	40·6	+419·2	+ 43	376·2	0·0029	0·0027	Feustel [6]
Aniline	45·0	+425·7	− 6·2	431·9	0·0025	0·0023	Renard and Guye [7]

Walden [8] has tested the above relationship for a considerable number of organic liquids. We see that the nearer the melting-point and critical temperature lie to one another, the greater is the temperature coefficient γ. In the case of the metals, for which $\theta_0 - t_0$ amounts to several thousand degrees, it is correspondingly small (about 0·0003; see Table 7).

We can of course calculate by means of the relation just discussed the critical temperature from γ. The values found, however, differ considerably from the experimental values.

This fact, and the fact that the agreement between γ (obs.) and γ (calc.) in Table 6 is only approximate, are due to the linear relationship between surface tension and temperature being true only at some distance from the

[1] Even below the melting-point the equation remains valid in accordance with the general rule that the properties of under-cooled liquids change in the same manner as the corresponding properties above the melting-point. This was proved for water down to − 8° C. by *Humphreys* and *Mohler* [Phys. Rev. **2**, 387 (1895)], and for a series of organic liquids by *Hock* (*loc. cit.* p. 22) and *Feustel* (*loc. cit.* p. 22).

[2] *loc. cit.* p. 25.

[3] Wied. Ann. **56**, 483 (1895).

[4] Ann. d. Physik (4), **17**, 749 (1905).

[5] *loc. cit.* p. 22.

[6] *loc. cit.* p. 22.

[7] Journ. chim. phys. **5**, 81 (1907).

[8] Zeitschr. f. physik Chemie, **65**, 129 (1909). *Walden* uses for σ_0 the surface tension at the boiling-point.

critical point. Close to the latter, the surface tension falls more slowly than the linear equation predicts; the σ, t line cuts the t axis not at the critical point, but at some degrees below it; the true σ, t curve approaches the critical point asymptotically.

Van der Waals also reaches this result in his theory of capillarity, and this is a notable advantage of his theory over Laplace's, which does not lead to this form of the σ, t curve in the neighbourhood of the critical point.[1] The formula which van der Waals deduces is valid at not too great a distance from the critical temperature θ_0 (which is now in degrees absolute), and is as follows:

$$\sigma = A\left(1 - \frac{T}{\theta_0}\right)^{\frac{3}{2}}.$$

A is a constant independent of the temperature. Not only is σ now equal to zero, when $T = \theta_0$, but $\frac{d\sigma}{dT}$ also vanishes; that is to say, the σ, T curve is tangential to the T axis at the critical point, as experience requires.

The numerical agreement of this formula with the measurements is not complete, but a formula

$$\sigma = A\left(1 - \frac{T}{\theta_0}\right)^{\xi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is well confirmed by them.[2] ξ appears to be about 1·23 for all liquids; A varies from liquid to liquid, and is not identical with the A of the theoretical equation.

So much may be said of the departure required by theory of the σ, t curve from linearity in the neighbourhood of the critical point. The assumption of linearity, and deduction of the temperature coefficient γ, are therefore only permissible at temperatures which lie sufficiently far below the critical temperature. Some regularities will now be considered, which are valid for the temperature coefficient γ.

The temperature coefficient of the surface tension of a liquid is closely connected with the dependence of its density upon temperature. The simple relationship holds *that the temperature coefficient of the surface tension is symbatic with the mean coefficient of cubical expansion.*[3] In the following table, the value of γ is followed by that of the coefficient of expansion $\varkappa$ and of the ratio $\frac{\gamma}{\varkappa}$. For the observers see Table 6; they are mostly responsible also for the values of $\varkappa$ given; only in a few cases are the latter taken from Landolt-Börnstein-Roth.

[1] See *van der Waals—Kohnstamm*, Lehrb. d. Thermodynamik, I. p. 218.

[2] Tested by *van der Waals* [Zeitschr. f. physik. Chemie, **13**, 716 (1894)], also by *Verschaffelt, loc. cit.* p. 25, and others.

[3] The terms "symbatic" and "antibatic" are derived from Greek words meaning "going with" and "going against." They are used to express the fact that two curves are more or less similar in form; when they are symbatic, they also follow the same course; when antibatic, the course of one is the reverse of that of the other. They are usually used in comparing the nature of the dependence of two different properties of a body upon a common variable, e.g. temperature. They originated in Germany (Nernst) and have not yet come into common use in English.—[Trans.].

TABLE 7

Temperature Coefficient of Surface Tension and Coefficient of Expansion

Substance.	γ	$\varkappa$	$\frac{\gamma}{\varkappa}$
Nitrogen	0·018	0·00558	3·2
Argon	0·013	0·00454	2·9
Carbon monoxide	0·013	0·00491	2·6
Cadmium [1]	0·00042	0·000170	2·5
Tin [1]	0·00027	0·000144	1·9
Mercury [1]	0·00035	0·000181	1·9
Lead [1]	0·00029	0·000129	2·2
Ethyl alcohol	0·0022	0·00106	2·1
Acetic acid	0·0038	0·00116	3·3
Benzene	0·0035	0·00139	2·5
Phenol	0·0029	0·00089	3·3
Aniline	0·0025	0·00092	2·7
Nitrobenzene [2]	0·0028	0·00089	3·1

This relationship, first emphasized by Cantor,[3] has also been tested by Walden [4] on a series of organic liquids.

It is noteworthy that this connexion may also be deduced from the Laplace theory, and that, as Cantor showed, Laplace [5] himself drew attention to it. According to Laplace

$$\sigma = 2\pi\varrho^2 \int_0^d x\psi(x)dx.$$

If we differentiate with respect to the temperature we have on the right-hand side only the differential coefficients,

$$\frac{d\varrho}{dt} \text{ and } \frac{dx}{dt} \text{ or } \frac{d\delta}{dt},$$

since the function $\psi(x)$ is regarded as independent of the temperature. But $\frac{d\varrho}{dt} = -\varkappa\varrho_0$ (ϱ_0 is the density at the temperature which is regarded as zero for the purpose of the calculation); $\frac{dx}{dt}$, the dependence of the radius of molecular attraction upon the temperature, is proportional to the coefficient of linear expansion, which is equal to $\frac{x}{3}$. The whole dependence upon temperature of the right-hand side may therefore be referred to the change in density with temperature. This differentiation of the Laplace equation with respect to t, and a few simple rearrangements, give the relation first put forward by Cantor: $\gamma = 2{\cdot}33\varkappa$. Table 7 shows that not only is $\frac{\gamma}{\varkappa}$ approximately constant, but also does not lie very far from 2·33. Bakker [6] has however pointed out correctly that, if we compare γ and $\varkappa$ at

[1] According to *Siedentopf, loc. cit.* p. 25.
[2] According to *Feustel, loc. cit.* p. 22.
[3] Wied. Ann. **47**, 421 (1892).
[4] Zeitschr. f. physik. Chemie, **65**, 129 (1909).
[5] Œuvres, Vol. IV. p. 505–506.
[6] Zeitschr. f. physik. Chemie, **86**, 157 (1914).

corresponding temperatures, e.g. the melting-point, the constancy of the ratio $\frac{\gamma}{\varkappa}$ is better, but its value lies considerably higher (about 3·7; molten metals were not taken into account by him).

As soon as we come to compare different liquids with respect to their surface tension, we must pay great attention to whether they are homogeneous; i.e. strictly contain only one kind of molecule. If this is not the case, and if there is in the liquid an equilibrium between different kinds of molecules, the possibility must always be taken into account, that the surface may have a different composition from that of the bulk of the liquid. We shall discuss this in detail later (p. 46). The comparison of such a liquid with a homogeneous one is not permissible without further question. How careful it is necessary to be is already clear from the relation between γ and $\varkappa$, for the symbasis between the two quantities is not present in the case of water. The anomaly in the density below 4° does not appear in the temperature coefficient of the surface tension.

Hence the discussion here and in the following paragraphs must be limited as far as possible to non-associated liquids; and it would further be preferable to start from the van der Waals and not from the Laplace theory of capillarity. R. O. Herzog [1] has taken both considerations into account. He deduced for non-associated liquids from the equation of van der Waals on p. 29, and from a relation given by Avenarius [2] between specific volume v and the temperature, a formula

$$\log_{10} \sigma = - \mathrm{m}v + \mathrm{n}.$$

Here m and n are constants, m being proportional to the critical density ϱ_k, while n is a more complicated function made up of the constants which appear in the initial equations. We can therefore calculate the surface tension for any temperature from the specific volume by means of this equation.

In the search for a relation between the thermal dependence of the surface tension and the composition of the liquid, the van der Waals theory of corresponding states has proved, as often before, of value, and has led to a rule which is valid for a large number of liquids. Van der Waals [3] and Kamerlingh Onnes [4] already recognized this fact in essence. Eötvös [5] arrived at a fully defined formula, which was then first tested by Ramsay and Shields [6] in detail.

For this purpose we reckon the temperature backwards from the point at which the σ, t line cuts the t axis, a point which, as mentioned above on p. 29, lies some degrees below the critical point, and we do not compare the surface tensions, i.e. the free surface energies per unit of surface, but the *molar free surface energies*, with one another. The molar free surface energy is the product of the surface tension and that surface which is developed by a molar amount (determined say from the vapour density) of the liquid considered as a sphere. If M is the molecular weight, v the specific volume, the molar surface is proportional to $(\mathrm{M}v)^{\frac{2}{3}}$. If we put, therefore, the molar surface and the temperature calculated in the above-mentioned manner into

[1] Zeitschr. f. Elektrochemie, **14**, 830 (1908).
[2] Beiblätter, **2**, 211 (1878).
[3] "Über die Kontinuität des gasförmigen und flüssigen Zustandes," p. 110.
[4] Koninkl. Akad. v. Wetensch. Amsterdam, **21**, (1881).
[5] Wied. Ann. **27**, 448 (1886).
[6] *loc. cit.* p. 27.

equation (1), p. 28, we get the equation of Eötvös, and Ramsay and Shields,

$$\mu = \sigma(Mv)^{\frac{1}{3}} = k(\theta_0 - T - \tau) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Here k is a constant, which is largely independent of the nature of the liquid. τ is the small amount (about 6°) which must be deducted from the critical temperature, in order to get the point at which the σ, t straight lines cut the t axis. It should be noted that the correction τ was not introduced by Eötvös, but first by Ramsay and Shields; Eötvös, on the other hand, desired (with a certain justification, as we shall see immediately) to limit the relation to liquids in corresponding states.

It is naturally by no means necessary, in order to determine k, to know θ_0 and τ. We need only measure σ for two different temperatures T_1 and T_2, eliminate θ_0 and τ, and get k from the equation

$$k = \frac{\mu_1 - \mu_2}{T_2 - T_1} = \frac{\sigma_1(Mv_1)^{\frac{1}{3}} - \sigma_2(Mv_2)^{\frac{1}{3}}}{T_2 - T_1}.$$

Table 8 shows how far the rule holds.

TABLE 8

Rule of Eötvös and Ramsay and Shields

Substance.	k.	Observer.
Nitrogen	2·00	Baly and Donnan [1]
Oxygen	1·92	,, ,,
Argon	2·02	,, ,,
Chlorine	2·10	Marchand [2]
Carbon monoxide	2·00	Baly and Donnan [1]
Silicon tetrachloride	2·03	Ramsay and Shields [3]
Sulphuryl chloride	2·16	,, ,,
Ethyl ether	2·17	,, ,,
Carbon tetrachloride	2·11	,, ,,
Carbon bisulphide	2·02	,, ,,
Benzene	2·10	,, ,,
Aniline	2·05	,, ,,
Nitrobenzene	2·23	,, ,,
Pyridine	2·23	,, ,,

The Eötvös rule has been tested in recent years by Walden,[4] Dutoit and Mojoiu,[5] Getman,[6] Merry and Turner,[7] Morgan,[8] F. M. Jaeger [9] and others.

[1] *loc. cit.* p. 25.

[2] Journ. d. chim. phys. **11,** 573 (1913).

[3] *loc. cit.* p. 27.

[4] Zeitschr. f. Elektrochemie, **14,** 713 (1908). Zeitschr. f. physik. Chemie, **65,** 129, 257 (1908); **66,** 385 (1909); **70,** 569 (1909); **75,** 555 (1910); Ion I. 402 (1909); *Walden* and *Swinne*, Zeitschr. f. physik. Chemie, **79,** 700 (1912); **82,** 271 (1913).

[5] Journ. d. chim. phys. **7,** 169 (1909).

[6] Am. Chem. Jour. **44,** 145 (1910).

[7] Journ. Chem. Soc. **97,** 2074 (1910).

[8] *loc. cit.* p. 21. Further, *Morgan*, Zeitschr. f. physik. Chemie, **78,** 129 (1912); *Morgan* and *Thomssen*, *ibid.* **78,** 148 (1912); *M.* and *Daghlian*, *ibid.* **78,** 169; *M.* and *Schwartz*, *ibid.* **78,** 185; *M.* and *Stone*, Journ. Am. Chem. Soc. **35,** 1505 (1913); *M.* and *Chazal*, *ibid.* **35,** 1821; *M.* and *Kramer*, *ibid.* **35,** 1834; *Morgan*, *ibid.* **37,** 1461 (1915).

[9] *loc. cit.* p. 22.

The result of these investigations may be summed up as follows. The Eötvös relation holds for a large number of liquids of not too great molecular weight, and which may be regarded for other reasons as non-associated. We can therefore calculate from it the molecular weight by means of the equation

$$M = \frac{1}{v}\left\{\frac{k(\theta_0 - T - \tau)}{\sigma}\right\}^{\frac{3}{2}}$$

or

$$M = \left\{\frac{k(T_2 - T_1)}{\sigma_1 v_1^{\frac{1}{3}} - \sigma_2 v_2^{\frac{1}{3}}}\right\}^{\frac{3}{2}}$$

as the case may be.

The value 2·12 for k is assumed as the most probable. Water, the alcohols and fatty acids,[1] molten salts,[2] and metals,[3] have much smaller values of k. In the case of water, even assuming double molecules, k increases from 1·59 between 3° and 40° to 2·27 between 150° and 210°.[4] Other substances, such as molten salts, for example, have much lower k values (around 0·6), which are, however, fairly constant. Whether association causes all these variations, or whether other influences should be taken into account, will be discussed on p. 37.[5]

k not only varies in the sense of being too small in the case of many substances. From the investigations of Dutoit and Friedrich,[6] Guye and Homfray,[7] Turner and Merry,[8] and Walden,[9] it would indeed appear that in the case of many liquids which are to be regarded as entirely normal, a regular rise of k occurs with rise of molecular weight. Values of k exceeding 5 were found in the case of substances of high molecular weight such as tripalmitine and tristearine. A dissociation is quite improbable; nor can it be detected by any other method. In the first place the fact must be taken into account that k is not strictly independent of temperature. In agreement with the view of Eötvös, liquids can only be compared at corresponding temperatures, and only at temperatures which lie more than half way between absolute zero and the critical temperature. This condition is not fulfilled for the substances of high molecular weight, with their much higher critical points, at the intermediate temperatures ordinarily used. In the case of these substances, also, k actually diminishes at higher temperatures, and approaches the ordinary value of about 2. (Cf. p. 36.)

If it is desired to compare these liquids at intermediate temperatures, k must be regarded as a function of the molecular weight; according to Walden and Swinne, the best plan is to regard k as a linear function of the expression $\Sigma\sqrt{A}$,

$$k = p + q\Sigma\sqrt{A}.$$

[1] *Morgan* and *McAfee*, Journ. Am. Chem. Soc. **33**, 1275 (1911).

[2] *F. M. Jaeger*, *loc. cit.* p. 22; *R. Lorenz*, *Liebmann* and *Höchberg*, Zeitschr. f. anorg. Chemie, **94**, 301 (1916).

[3] *Bottomley*, *loc. cit.* p. 26; *R. Lorenz* and *Kaufler*, Ber. d. deutsch. chem. Ges. **41**, 3727 (1908).

[4] *Eötvös*, Wied. Ann. **27**, 458 (1886).

[5] Among the crystalline liquids there are some, such as *p*-anisole-azophenolethyl carbonate, which have a normal constant, while others, such as *p*-acetophenone-azophenetole and *p*-acetophenone-azophenolethyl carbonate, prove to be associated. (*E. Schaefer*, Untersuchungen über Dichte, Reibung und Kapillarität kristallinischer Flüssigkeiten. Diss. Halle, 1911.)

[6] Arch. sci. phys. et nat. **9**, 16 (1900).

[7] Journ. d. Chim. phys. **1**, 505 (1904).

[8] Journ. Chem. Soc. **97**, 2069 (1910).

[9] Zeitschr. f. physik. Chemie, **75**, 555 (1911).

Here A is the atomic weight, p and q are constants, and the summation is to be extended over all elements which go to compose the molecule.

Many and various attempts have been made to discover other colligative relationships for the surface tension, which may be strictly valid for the non-associated liquids, but show regular deviations for the associated ones. In most cases the initial point is the fact that the free surface energy is closely connected with the internal latent heat of evaporation. This at once appears probable when we consider that the latter also becomes zero at the critical point. Stefan [1] then showed that, starting from the Laplace point of view, the work which is necessary to bring a liquid molecule to the surface may be put equal to that which is necessary to bring it out of the surface into the vapour space; an idea to which, however, objections may be raised. The first work may be put equal to the molar free surface energy, the second to the molar latent heat of evaporation, and a proportionality may be obtained between the two quantities. If it be remembered that a colligative relation is already known for $M\lambda_s$, the molar latent heat at the boiling-point, namely the Trouton rule,

$$\frac{M\lambda_s}{T_s} = \text{Const.},$$

then it is easily understood that colligative regularities may also be deduced in this way for the surface tension; this may be done directly for temperatures to a large degree corresponding, namely the boiling-points.

Account has also been taken of the fact that according to Nernst the Trouton rule must be altered to remain valid at low temperatures.[2]

Kistiakowsky,[3] Walden,[4] and Dutoit and Mojoiu [5] have discussed the matter from this point of view. These equations are in so far successful, as they ascribe normal behaviour to a number of bodies of high molecular weight for which bodies Eötvös formula gives k values which are too large. The range of application of such equations remains none the less necessarily limited; above all, a conclusion as to the degree of association is never certain. For if more than one kind of molecule be present, the surface layer has generally a different composition from the mass (see p. 46); an equation, therefore, which holds for the surface tension does not necessarily tell us anything about the association of the liquid itself.

Certain thermodynamical considerations enable us to recognize what the constancy or non-constancy of $\frac{d\sigma}{dT}$ or $\frac{d\mu}{dT}$ actually means. It was already mentioned on p. 6 that the expression σw does not give the whole change of energy accompanying increase of surface; σw is only the mechanical work done, the change of free energy, therefore. The change in total energy and free energy are of course only equal when the latter is independent of the temperature. This is by no means the case here, since σ alters with temperature. The relation between the change in total energy

[1] Wied. Ann. **29**, 655 (1886); see also *Brandt*, Ann. d. Physik. (4) **10**, 783 (1903), and *Kleeman*, Phil. Mag. (6), **21**, 83, 352 (1911); **22**, 566 (1911).
[2] *Walden*, Zeitschr. f. physik. Chemie, **65**, 257 (1908).
[3] Zeitschr. f. Elektrochemie, **12**, 513 (1906).
[4] Zeitschr. f. physik. Chemie, **65**, 129 (1908).
[5] *loc. cit.* p. 32.

U and in the free energy $A_\omega = \sigma\omega$ is obtained by applying the thermodynamical equation for a reversible change.[1]

$$A - U = T\frac{dA}{dT}$$

and putting $A = \sigma\omega$.

We get

$$U_\omega = \sigma\omega - T\frac{d\sigma}{dT}\omega,$$

and calculated on the unit of surface

$$u_w = \sigma - T\frac{d\sigma}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This is the *total surface energy* per unit of surface, while σ is the *free surface energy* per unit of surface. Correspondingly

$$\left(\sigma - T\frac{d\sigma}{dT}\right)(Mv)^{\frac{2}{3}}$$

is the *molar total surface energy*,[2] and

$$\mu = \sigma(Mv)^{\frac{2}{3}}$$

is the *molar free surface energy*.

The expression $q_\omega = T\frac{d\sigma}{dT}$ has the character of a heat change. It is the *latent surface heat* per unit of surface, as it may be called by analogy with the latent heat of evaporation and of a chemical reaction. Since $\frac{d\sigma}{dT}$ is negative, q_ω has also a negative sign. From equation (4) it then follows that if heat be developed, energy is also given up; that is to say, the surface contracts; *cooling and absorption of heat must therefore result from an increase of surface.*

[1] Here, as throughout this book, the "egoistic" standpoint is assumed; that is to say, energy, work, and heat, which are supplied to a system, are reckoned negative, and when abstracted, positive. This corresponds to the notation used by *Haber* in his "Thermodynamics of Technical Gas Reactions." *Nernst*, in his "Theoretical Chemistry," reckons energy and work in the same sense, heat in the opposite.

[2] Many attempts have been made to make use of the total surface energy as a characteristic quantity. For example, *Whittaker* [Proc. Roy. Soc. **81**, 21 (1908); see also *Kleeman*, Phil. Mag. (6), **18**, 39, 491, 901 (1909); *Mills* and *McRae*, Journ. Am. Chem. Soc. **32**, 1162 (1910); *Bennett* and *Mitchell*, Zeitschr. f. physik. Chemie, **84**, 475 (1913)] deduced a relation between this quantity, the latent heat, and the absolute temperature. *Swinne* [Zeitschr. f. physik. Chemie. **79**, 461 (1912)] shows, however, that if the *van der Waals* equation (2) on p. 29 for the dependence of surface tension upon temperature is valid, and if we are dealing with relations existing between σ and other quantities at corresponding temperatures, then the same relations must be valid also for the total surface energy $\left(\sigma - T\frac{d\sigma}{dT}\right)$. At corresponding temperatures, as *Kleeman* has already pointed out in another connexion [Phil. Mag. (6), **18**, 495 (1909)], the ratio $\frac{\sigma - T\frac{d\sigma}{dT}}{\sigma}$ is constant.

From equation (4) a relation to the specific heat at constant volume c_v may be deduced, following Einstein [1]; this is

$$\frac{dc_v}{d\omega} = -T\frac{d^2\sigma}{dT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If now the σ, T curve is linear, if therefore $\frac{d\sigma}{dT} = \gamma = \text{Const.}$, then $\frac{d^2\sigma}{dT^2} = 0$ and hence $\frac{dc_v}{d\omega} = 0$; that is to say, *the specific heat of the liquid is independent of the size of the surface*; the surface layer has not a characteristic specific heat of its own, but the same as for the liquid in bulk. The molecular movement is hence the same there as in the interior of the liquid, the free surface energy is entirely static, not kinetic. On account of the connexion discussed on p. 29 between surface tension and density it follows that also $\frac{d\mu}{dT} = \text{Const.}$, if $\frac{d\sigma}{dT} = \text{Const.}$ The constancy of k in Eötvös' formula means therefore that the surface layer has the same specific heat as the bulk of the liquid.

If however the σ, T curve is bent, and $\frac{d\sigma}{dT}$ or $\frac{d\mu}{dT}$ variable, then the specific heat of the surface layer differs from that of the liquid in bulk. This may depend upon a displacement of the associative equilibrium between the different kinds of molecules, assuming that k is too small and increases with rise of temperature. Cases are however known, as that of acetic acid,[2] in which a low, practically constant k and a decrease of polymerization with rise of temperature occur together. Perhaps the surface layer consists, over the whole range of temperature investigated, of the one kind of molecule exclusively.[3]

If, on the other hand, k is variable, but too great (as in the case of substances of high molecular weight, see p. 33), association cannot be the cause of the characteristic specific heat of the surface layer. But if the molecules of the substances of high molecular weight have a particular shape, perhaps long and thin, as may be regarded as not improbable for many of these substances,[4] then the molecular-kinetic conditions may very well be other in the surface layer than in the interior of the liquid. For the gradient of density in the surface layer causes the number of molecular impacts from the direction of the interior of the liquid to be greater than the number from the less dense side towards the vapour. A long and thin molecule lying in the surface layer would therefore not be in equilibrium, if it lay with its longer axis in the surface plane; it would strive to set itself at right-angles to this plane. In the case of liquids with elongated molecules, therefore, we must expect the latter to have a preferential position in the surface layer, namely, with their long axes at right-angles to the surface. In the case of liquids with disc-shaped molecules, these should set themselves in the surface layer with their planes at right-angles to the surface. The surface energy would thus necessarily

[1] Ann. d. Physik. (4), **4**, 513 (1901).
[2] *Eötvös*, Wied. Ann. **27**, 459 (1886).
[3] See *F. M. Jaeger*, Koninkl. Akad. v. Wetensch. **17**, 419 (1914).
[4] See the investigations, discussed later on p. 317, of *Langmuir*, who was the first to deduce an elongated form for such molecules on grounds taken from capillary chemistry.

have a kinetic part, and the dependence of the specific heat upon the size of the surface and the variability of k would be comprehensible.[1]

Whether the case of molten salts and metals, in which k is too small, but constant, can be explained in a similar manner to the case of acetic acid mentioned above, appears questionable. In the case of liquids of such a totally different type—all the substances in question are good conductors of electricity—it cannot be known beforehand whether the fundamental assumption of the Eötvös formula, the law of corresponding states, is applicable.

We shall have to wait for a kinetic theory of liquids to explain their behaviour. As is well known, we cannot form so clear a picture of a liquid's molecular structure as we can in the two limiting cases of rarefied gases, and of a certain group of crystalline solids. The subject may be briefly discussed here, since it is also of importance for other questions.

Experience has confirmed the kinetic theory for rarefied gases to a large degree. A gas consists of small particles which are in rapid motion, and collide elastically with one another. In the case of such gases as the inert gases and metallic vapours, the smallest particles are atoms, in other cases molecules containing two or more atoms. The atoms are built up, according to the theory of Rutherford and Bohr, of extremely small positive nuclei (radius about 2×10^{-13} cm.), around which electrons rotate in circular or elliptical orbits, the total charge of the electrons being just large enough to balance the positive charge of the nucleus.[2] The number of electrons, and hence the charge of the nucleus, is equal to the *atomic number* of the element; thus hydrogen with atomic number 1 has a nucleus with charge 1 around which one electron rotates. Helium with an atomic number 2 has a nucleus with charge 2, around which two electrons rotate. The paths in which the electrons move are determined by the quantum equations which Bohr applied to the structure of atoms. They are hence described as quantum orbits. In this way not merely one quantum orbit—if we take the case of hydrogen as an example—at the shortest possible distance from the atom is determined, but the atom may also exist in other forms richer in energy, in which the electron does not rotate in this 1-quantum orbit,

[1] *Born* and *Courant* arrive at another explanation of the excessive k values [Physik. Zeitschr. **14**, 731 (1913); see also *Madelung*, Physik. Zeitschr. **14**, 729 (1913)]. They apply to the oscillations of the molecules in the surface layer of the liquid considerations which were first applied by *Debye* [Ann. d. Physik (4), **39**, 789 (1912)] to the oscillations of the molecules of solid bodies. They regard these oscillations as elastic, and hence the velocity of sound in the liquid enters into their discussion as an important quantity. *Born* and *Courant* thus arrive at a formula, which contains the *Eötvös* formula as a special case. The expression corresponding to k in the *Eötvös* formula, a function of the velocity of sound in the liquid, assumes a value, when certain assumptions are made, which is very close to k. The excessive values of k for substances of high molecular weight would then be explicable on the grounds that these large molecules do not simply oscillate as a whole, but that certain groups of atoms present in the molecule have also a definite freedom to vibrate (see also *Nernst*, "Theoretical Chemistry," 7th edition, p. 298 of original, or Tizard's English translation, concerning the necessity for taking molecular-kinetic influences into account in deducing the connexion between free surface energy and latent heat of evaporation). Attention may also be drawn here to the *Debye* theory of surface tension and its dependence upon temperature, at which he arrives by the supposition that the *van der Waals* attraction is a result of electric forces [Physik. Zeitschr. **21**, 178 (1920); cf. also p. 128].

[2] For a general view of this subject see *Sommerfeld*, "Atombau und Spektrallinien," Braunschweig, 1919, trans. into English by H. A. Brose (Methuen, London, 1922); *Loring*, "Atomic Theories," London, 1921.

but in orbits of 2, 3, or more quanta. The energy which is set free, when the electron falls from an orbit of higher quantum value into one of lower quantum value, is radiated as light ; and the reason why the Bohr atom has become of such paramount importance is, that it is possible to explain numerically a great many spectra by means of it. From the various atomic forms thus distinguished by different energy content we must distinguish the continuous change which the quantum orbits of an atom undergo through an external electric field on account of the *Stark* effect : the atom passes in this case into a less stable form. Since every atom produces an electrical field in its neighbourhood, the compression of a monatomic gas alone suffices to bring about this continuous change in the quantum orbits.

In diatomic molecules the atoms are so bound to one another that the nuclei of the two atoms are held together by the electrostatic forces, which are exerted by the electrons moving in changed quantum orbits. It has not hitherto been possible to imagine the structure of the simplest gas molecule, that of hydrogen, correctly to the extent of explaining completely all the properties of gaseous hydrogen. From this fact may be judged the difficulties which arise in the case of other substances and of molecules with a larger number of atoms. Only in the case of rarefied gases and not too high temperatures are almost all molecules of the gas present in the most stable form. At higher pressures and temperatures, as a result of the electric field between the closely packed molecules and of the collisions between them, more and more of them will be present in a less stable form ; the same changes in the quantum orbits must be reckoned with as have just been discussed for the case of atoms.

Since a liquid always corresponds to a compressed gas, we must assume the presence in it of less stable molecules in sensible amount ; and this renders it explicable—since the unstable molecules are more reactive than the stable—that a reaction takes place much more energetically in a liquid than in its vapour. This will be particularly true of liquids in which strong electric fields are present, that is to say, those with a high dielectric constant.

In fact, the question may be asked, how far is the molecular combination maintained in a liquid ? Is there perhaps a lively exchange of atoms from molecule to molecule ? This question suggests itself when we compare the liquid with the solid state. As mentioned, the kinetic theory has explained not only the state of a rarefied gas, but also to a large extent the state of a group of crystalline solids, which are termed *heteropolar*. To this group belong substances such as salts, oxides, etc., in which atoms or atomic groups of electrically opposite behaviour may be easily distinguished. A sodium chloride crystal may be taken as the type of a solid heteropolar body. On the other hand, the diamond, for example, is homoiopolar, in which no such distinction is possible off-hand. It has been found possible to explain the state and the properties of solid sodium chloride to a considerable extent upon the view that the sodium and chlorine atoms occupy alternately the points of a cubical space lattice and execute vibrations about these points. The molecular combination is therefore dissolved ; a chlorine atom is not merely combined with a sodium atom, but six sodium atoms are equally near to it ; it is influenced by all the atoms of the NaCl crystal, so that we may if we wish regard the whole crystal as a molecule. How far the behaviour of homoiopolar substances is similar, is still unsettled.

We might therefore be tempted to assume also for liquids that the

molecular combination is dissolved, and that the atoms continually break up old combinations and enter into new ones.[1] For molten salts this view is certainly the more probable. In the case of liquids, on the other hand, such as the hydrocarbons and such-like, it is a more probable assumption that, as in the gaseous state, the molecular combination to a great extent remains in existence. Liquids such as water occupy an intermediate position. In contrast to gases, polar properties are to be ascribed to the molecules of all liquids, including the liquid hydrocarbons; they are to be regarded as dipoles, and this the more so, the higher the dielectric constant. Water takes up, in view of its high dielectric constant of about 80, a remarkable position as compared with all other liquids.

That the molten salts occupy a position of prominence with respect to the rule of Eötvös is certainly connected with the fact that in their case, as highly conducting liquids, in contrast to the others, which mostly have a much smaller conductivity, the molecular combination is dissolved to a large degree.

From equation (4) it further follows, if we differentiate with respect to T and only consider a linear part of the σ, T curve,

$$\frac{du_\omega}{dT} = \frac{d(\sigma - q_\omega)}{dT} = -T\frac{d^2\sigma}{dT^2} = 0 \quad . \quad . \quad . \quad . \quad . \quad (6),$$

that is, *the total surface energy is independent of the temperature.* In the neighbourhood of the critical point, where the σ, T curve is no longer linear, we have to reckon with a special thermal capacity of the surface, and a dependence of the whole surface energy on the temperature. A test of the last-mentioned relation by Whittaker, which was confirmed in the main by Bennett and Mitchell,[2] showed that departures from formula (6) occur already at a considerable distance from the critical point.

Remembering that, according to Nernst's Heat Theorem,

$$\frac{dU}{dT_{\lim T=0}} = \frac{dA}{dT_{\lim T=0}} = 0,$$

it follows from equation (6) for the neighbourhood of absolute zero that

$$\sigma = q_\omega \text{ and } \frac{d\sigma}{dT} = \frac{dq_\omega}{dT} = 0.$$

The entire course of the σ, T curve therefore corresponds[3] to that illustrated in Fig. 9. First, starting from T = 0, a piece parallel to the T axis; then a descending part mainly linear; and finally an asymptotic approach at the critical point.

The thermodynamic considerations here discussed were first put forward by W. Thomson,[4] and then extended in various directions by van der Waals,[5] Cantor,[6] Pellat,[7] Einstein,[8] Parks,[9] and others,[10] in some cases independently of one another.

[1] *Langmuir* [Journ. Am. Chem. Soc. **39,** 1857 (1917)] prefers this view for the liquid state in general.

[2] *loc. cit.* p. 35.

[3] *Nernst,* "Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes," p. 176 (1918).

[4] Phil. Mag. (4), **17,** 61 (1859).

[5] *loc. cit.* p. 11.

[6] *loc. cit.* p. 22.

[7] Compt. rend. **118,** 1193 (1894).

[8] *loc. cit.* p. 36.

[9] Phil. Mag. (6), **4,** 240 (1902).

[10] See also the critical discussion by *Bakker* (Zeitschr. f. physik. Chemie, **68,** 684 (1910)].

In the case of the relations between surface tension, temperature, and chemical composition already treated, colligative connexions in particular were found. In the equations in question there is found, together with an expression containing the surface tension, one in which the critical temperature or the absolute boiling-point occurs. If it is wished to find relations between the surface tension of a compound and its chemical composition alone, under comparable conditions (a course which naturally suggests itself in the case of a great number of organic compounds), then it follows from the results above attained that the surface tension will follow similar laws to the critical temperature or absolute boiling-point. For it would be otherwise impossible that in an equation containing both, the specific should disappear, and the colligative remain. Since the dependence of the critical temperature or the absolute boiling-point of a compound upon its composition has an additive character, with a distinct constitutive tendency, the same is to be expected for the surface tension.

The first question which arises is, what function of the surface tension should be used, in order to avoid the uncertainty introduced by the variation

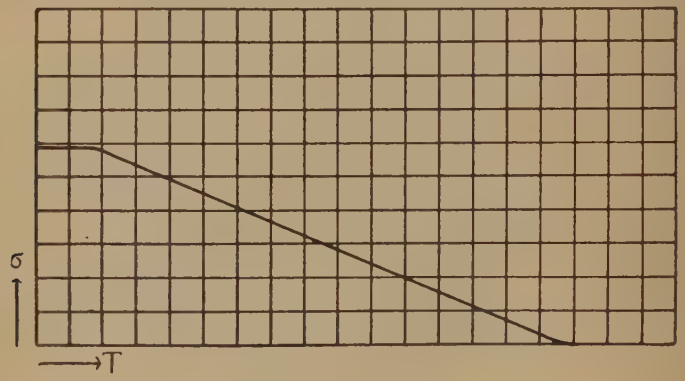


Fig. 9. σ, T Curve.

of σ with temperature. Various courses are open: either the liquids may be compared at corresponding temperature, such as the boiling-points, as was done by Schiff,[1] or a function as far as possible independent of the temperature is used, such as the total surface energy (see p. 39) or an expression derived from it. Thus Bennett and Mitchell [2] made use of the molar total surface energy

$$\left(\sigma - T\frac{d\sigma}{dT}\right)(Mv)^{\frac{2}{3}},$$

while Einstein [3] made use of a function of this expression

$$Mv\sqrt{\sigma - T\frac{d\sigma}{dT}}.$$

Since the total surface energy is still sensibly dependent upon the temperature (see p. 39), Kleeman [4] prefers a quantity in which the dependence of the total surface energy upon the temperature is taken into account.

[1] Lieb. Ann. **223,** 47 (1884); Mem. d. R. Accad. d. Lincei (3), **19,** 64 (1884).
[2] *loc. cit.* p. 35. [3] *loc. cit.* p. 36.
[4] Phil. Mag. (6), **18,** 491, 901 (1909). See also *Walden*, Zeitschr. f. physik. Chemie, **66,** 385 (1909); *Walden* and *Swinne*, *ibid.* **79,** 700 (1912).

In order to obtain a general view of the behaviour of the surface tension, not in order to recommend the function used over others, we may discuss shortly the results of Bennett and Mitchell. The molar total surface energy employed by them

$$U_\omega = \left(\sigma - T\frac{d\sigma}{dT}\right)(Mv)^{\frac{2}{3}}$$

can only be used as characteristic function in the case of the non-associated liquids, since only in their case is it sufficiently independent of the temperature ; in the case of associated liquids such as the alcohols, fatty acids, and other liquids, U_ω increases in general greatly with increase of temperature. The U_ω of a compound may be calculated additively to a great extent from atomic values. A constitutive influence is very distinct ; the double bond must be taken into account, ethereal oxygen distinguished from carbonyl oxygen, and so on. How far the agreement goes is shown by the following extract from the table of Bennett and Mitchell.

TABLE 9

Stoichiometrical Behaviour of the Molar Total Surface Energy

H = 310 C = − 537 } CH_2 = 83	N (Amines, etc.) = 0	Cl = 465	
O (ether, etc.) = 160	CN = 550	Br = 600	
O (ketone) = 780	CNS = 870	J = 805	
	NCS = 945	NOH = 820	
		NO_2 = 700	

Hexamethylene ring closure	= 740
Pentamethylene „ „	= 717
Trimethylene „ „	= 671
Double bond . . .	= 654
C_6H_5	= 996

	U_ω (obs.).	U_ω (calc.).	Observer.
n-Hexane, C_6H_{14}	1,190	1,118	Dutoit and Friderich [1]
Toluene C_7H_8	1,350	1,383	Ramsay and Aston [2]
m-Xylene, C_8H_{10}	1,465	1,466	„ „
Ethyl formate, $C_3H_6O_2$ . . .	1,140	1,189	„ „
Methyl acetate, $C_3H_6O_2$ . . .	1,170	1,189	„ „
Methyl benzoate, $C_8H_8O_2$ . .	1,780	1,786	Renard and Guye [3]
Propyl hydrocinnamate $C_{12}H_{16}O_2$	2,090	2,118	Walden and Swinne [4]
Diethyl ether, $C_4H_{10}O$ . . .	1,105	1,112	Ramsay and Shields [5]
Nitrobenzene, $C_6H_5NO_2$ . . .	1,690	1,690	„ „
Acetone, C_3H_6O	1,050	1,029	„ „
Chloroform, $CHCl_3$	1,205	1,168	Ramsay and Aston [2]
Carbon tetrachloride, CCl_4 . .	1,295	1,323	Ramsay and Shields [5]

Schiff, Einstein and Kleeman arrive at similar results with their different types of functions.

As regards *inorganic liquids*, the σ values of the simplest compounds, such as H_2O, SO_2, etc., are entirely characteristic, and cannot easily be

[1] *loc. cit.* p. 25. [2] *loc. cit.* p. 27. [3] *loc. cit.* p. 28.
[4] *loc. cit.* p. 32. [5] *loc. cit.* p. 27.

connected with the properties of the constituent elements; a peculiarity which is of course generally true for the simplest compounds.

In the case of the *molten salts*, a certain *additive* dependence upon the radicals composing them is unmistakable. This is seen from Table 10, in which, on the basis of the measurements of F. M. Jaeger,[1] the σ values for a considerable number of salts at 1000° have been calculated.

TABLE 10

Surface Tension of the Alkali Salts at 1,000°

	F.	SO_4.	Cl.	Br.	NO_3.	J.
Li	237	215	110	—	74·7	—
Na	200·5	188	100	88·7	77·4	70·2
K	132	149·5	81·2	70·2	63·3	57·9
Rb	107·5	140	74·2	69·3	57·2	56·4
Cs	83·5	114	64·6	60·3	43·2	52·7

The series

$$F > SO_4 > Cl > Br > NO_3 > I$$

and

$$Li > Na > K > Rb > Cs$$

are worthy of note, since they are met with again in the most various phenomena, as will be described later (see p. 58). The CNS group follows with small σ values upon the iodides, as may be estimated from Table 4. The values for the alkaline earth, earth, and heavy metals lie mostly higher than those for lithium.

It is undoubtedly true that the elements can be arranged according to their surface tension in a periodic series. More extended measurements in this direction are not available, but for the compressibility, which is of course antibatic to the surface tension (see p. 43), Th. W. Richards [2] has proved a similar regularity.

The Relation of the Surface Tension to Internal Pressure, Compressibility, and Allied Quantities

If we look for relations of the surface tension to other properties of a liquid at a given temperature, we may be guided by the idea expressed above that the surface tension is closely connected with the internal pressure. According to considerations put forward by Walden,[3] which in part start from the ideas of Stefan mentioned on p. 34, the values of the internal pressure in atmospheres for non-associated liquids at the boiling-point may be calculated by multiplying the surface tension at the boiling-point by the proportionality factor 75.

Since according to van der Waals the internal pressure is proportional to the *critical pressure* in corresponding states, it follows that there is a parallelism between the surface tension in corresponding states (e.g. the boiling-point) and the critical pressure; according to Walden the critical

[1] *loc. cit.* p. 22.
[2] Zeitschr. f. Elektrochemie, **13,** 519 (1907).
[3] Zeitschr. f. physik. Chemie, **66,** 385 (1909).

pressure may be got from the surface tension at the boiling-point by multiplication by 2·22.[1]

The antibasis between surface tension and compressibility is noteworthy. It is particularly striking if we start from a point of view of Tammann's.[2] According to Tammann we may without question put the action of the external pressure equal to that of the internal pressure; a liquid with a high internal pressure, and hence a high surface tension, has therefore properties, as if it were under high external compression. Now the compressibility diminishes with increase of external pressure; hence according to Tammann it must diminish with increase of internal pressure, that is to say, it must be the smaller from liquid to liquid, the greater the internal pressure, the greater therefore the surface tension. Thus we get the antibasis of compressibility and surface tension. How far it is present is shown by Table 11; in it the compressibility $\beta \times 10^6$ for the pressure of one atmosphere is compared with the surface tension. The temperature is 25°, excepting in the case of mercury, water, and glycerine. In the case of the first it is 0°, and of the two latter 20°.

If we form the product $\sigma\beta \times 10^6$, it is not constant, but is in all cases of approximately the same order of magnitude. Water particularly, and the substances such as glycerine and others containing hydroxyl, show a great deviation; a sign that here, as always, association must be taken special account of. Th. W. Richards and Mathews [3] have put forward a relation $\beta\sigma^4 = \text{Const.}$, which agrees satisfactorily in the case of a number of normal organic liquids; the range within which the values of σ lie is, however, small (between 20 and 40 dyne/cm.).

TABLE 11

Surface Tension and Compressibility at 25° C.

Substance.	σ.[4]	$\beta \times 10^6$.	Remarks.
Mercury	440	3·83 [5]	$t = 0°$
Water	72·7	48 [6]	$t = 20°$
Ethyl alcohol	21·6	105 [7]	—
Glycerine	65	25 [8]	$t = 20°$
Ethyl ether	15·9	190 [7]	—
Acetone	23·3 [7]	121 [7]	—
Acetic acid	23·0	88 [7]	—
Chloroform	26·8 [7]	103 [7]	—
Carbon disulphide	32·7	90 [7]	—
Benzene	28·3	92 [7]	—
Aniline	43·2	46 [7]	—
Nitrobenzene	41·2	49 [7]	—

[1] A strict proportionality would only be present, if the radius of molecular action were equal for all substances. Since it is not so, but on the contrary proportional to the size of the molecule (c.f. p. 308), the simple relation between surface tension and critical pressure can only be valid if the molecules of the liquids compared are not too different in size (see *van der Waals*, "Kontinuität des gasförm. und flüss. Zustandes," Leipzig, 1881, p. 166).

[2] Zeitschr. f. physik. Chemie, **11**, 676 (1893); **13**, 174, 543 (1894); **14**, 163, 433 (1896); **16**, 91, 139, 659 (1895); **17**, 620, 725 (1895); **21**, 529, 537 (1895).

[3] Zeitschr. f. physik. Chemie, **61**, 449 (1908). [4] Mainly from Table 6.

[5] *Th. W. Richards*, Zeitschr. f. physik. Chemie, **61**, 171 (1908).

[6] *Amagat*, Ann. de chim. et de phys. (6), **29**, 68, 505 (1893).

[7] *Ritzel*, Zeitschr. f. physik. Chemie, **60**, 319 (1904).

[8] *Quincke*, Wied. Ann. **19**, 401 (1883).

The relation between surface tension and compressibility has also been pointed out by van der Waals,[1] Röntgen and Schneider,[2] Einstein,[3] and others.

As Geffcken [4] and Ritzel [5] especially have shown, the compressibility is closely related to the power of a liquid to dissolve difficultly soluble substances. As is well known, we can, in the case of such substances as the indifferent gases (the inert gases, hydrogen, nitrogen, carbon monoxide, and others) speak of a definite solvent power of the liquid. Independently of the nature of the solute, the liquids arrange themselves in the same order as regards solubilities. Since this solvent power and the compressibility run parallel to one another throughout, it is not surprising that the solvent power is antibatic to the surface tension, a fact to which Skirrow [6] and Christoff [7] have drawn attention.

Walden [8] has then further attempted to get a closer relation between the surface tension and the internal pressure, or, more generally, the quantities a and b of the van der Waals equation. Walden has also brought the *dielectric constant* into connexion with the surface tension on the basis of the Clausius-Mosotti equation; they run mostly symbatically.

Summing up, we may say that the *surface tension is symbatic to the internal pressure, the critical pressure, and the latent heat of evaporation, and antibatic to the compressibility and solvent power.*

Surface Curvature and Vapour Pressure

A relation of importance for colloidally disperse systems holds between the surface tension and the vapour pressure of curved liquid surfaces. Small and therefore strongly curved drops have a higher vapour pressure than large ones. This is self-evident when we consider that they do not represent a stable system, but must strive to reduce their surface by uniting to form one large drop. Upon direct contact they flow together; if they do not touch, the union must take place by evaporation. It is well known that if we take a vessel with a dew of liquid upon the interior, evacuate and seal it up, the small drops unite after some time to one large drop. Such experiments, however, have hitherto hardly been carried out with such constancy of temperature that the possibility of distillation from a warmer to a cooler point was excluded.

The thermodynamic relation between vapour pressure and surface curvature of a liquid was first deduced by W. Thomson.[9]

Two spherical drops of a liquid of density ϱ_f have the radii r_1 and r_2, the weights w_1 and w_2, and the vapour pressures p_1 and p_2. If the quantity dw is transferred from the first drop to the second, surface work is gained in the case of the first, and done in the case of the second. The two amounts of work are $\sigma d\omega_1$ and $\sigma d\omega_2$; the surface work done is $\sigma(d\omega_1 - d\omega_2)$. The

[1] "Über die Kontinuität des gasförmigen u. flüssigen Zustandes." Leipzig, 1881.
[2] Wied. Ann. **29,** 165 (1886).
[3] *loc. cit.* p. 36.
[4] Zeitschr. f. physik. Chemie, **49,** 257 (1904).
[5] *loc. cit.* p. 43.
[6] Zeitschr. f. physik. Chemie, **41,** 139 (1902).
[7] Zeitschr. f. physik. Chemie, **53,** 321 (1905); **55,** 622 (1906).
[8] Zeitschr. f. physik. Chemie, **66,** 385 (1909).
[9] Phil. Mag. (4), **42,** 448 (1881); see also *R. v. Helmholtz,* Wied. Ann. **27,** 508 (1886), whose deduction is followed in the text.

values of $d\omega_1$ and $d\omega_2$ are dependent upon the amount of change in the size of the surface with change in the size of the drop ; hence

$$d\omega_1 = \frac{\delta\omega_1}{\delta w_1} dw \text{ and } d\omega_2 = \frac{\delta\omega_2}{\delta w_2} dw.$$

If we introduce ω_1, ω_2, w_1 and w_2 as functions of r_1 and r_2, we get for the surface work

$$\frac{2\sigma}{\varrho_f}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) dw.$$

To complete the cycle, the amount dw is to be distilled back from the second to the first drop. This work of distillation amounts to

$$\frac{RT}{M} \log \frac{p_2}{p_1} dw,$$

where M is the molecular weight of the vapour.

Since the cycle is isothermal, the sum of the two amounts of work must be zero : we get therefore

$$\frac{RT}{M} \log \frac{p_2}{p_1} = \frac{2\sigma}{\varrho_f}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The expression is positive, when $r_2 < r_1$; $p_2 > p_1$, or, *the smaller drop has the larger vapour pressure.*

The formula becomes simpler when we compare, not two drops, but a drop and a plane surface ; r_1 will then $= \infty$, and $p_1 = p$, the normal vapour pressure of the liquid. We then get

$$\frac{RT}{M} \log \frac{p_2}{p} = \frac{2\sigma}{\varrho_f r_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we put for p_2 and r_2, p_ω and r respectively, and develop the left-hand side,

$$\log \frac{p_\omega}{p} = \log\left(1 - \frac{p - p_\omega}{p}\right) = \frac{p_\omega}{p} - 1,$$

we get

$$p_\omega = p + \frac{2\sigma p M}{RT\varrho_f r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If we further note that according to the gas laws $\frac{pM}{RT} = \varrho_d$, the density of the vapour, we get the Thomson equation

$$p_\omega = p + \frac{2\sigma\varrho_d}{\varrho_f r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which tells us by how much the vapour pressure of a drop of radius r exceeds the vapour pressure of a plane surface.

This is true for a convex surface ; for a concave one of the same radius of curvature r, the vapour pressure is smaller by the same amount. For a liquid in a capillary tube and a plane surface must be in equilibrium, and hence the vapour pressure at the surface in the capillary tube must be less than that at the plane surface by the weight of a column of vapour equal to the height of rise.

This change in vapour pressure only makes itself felt at very strong curvatures. If a drop of water has a radius of 10^{-4} cm., its vapour pressure is only about $^1/_{1000}$ greater than that of a plane surface. The rise of pressure only becomes considerable in the region of colloid dispersity.

In the case of a drop-radius of 10^{-6} cm., the vapour pressure would become 10 per cent. greater, and 10^{-7} 100 per cent. greater.

We must however take into account the fact that for such small drops the surface tension has a lower value than for larger ones. For as soon as the drop-radius falls within the order of magnitude of the radius of molecular action, or is even smaller, the work required to bring a molecule from the interior of the liquid to the surface becomes smaller, since the number of attracting molecules is smaller than in the case of the completely filled sphere of action which we consider in the case of a larger quantity of liquid. How great the diminution of the surface tension thus brought about may be, cannot be found with certainty, since it depends upon the law which governs the relation of distance to attraction for molecules: the law, that is, which has to be introduced for $\psi(x)$. This diminution of the surface tension is certainly not great, since the falling off of molecular attraction with distance is certainly very rapid.[1]

The Surface Properties of Solutions: Adsorption

When we now speak of solutions, we must consider a second substance being dissolved in the liquid phase, as well as more than one substance being present in the gas space. It is of fundamental importance for the surface properties of a solution that the composition of the surface layer is mostly different from that of the solution in bulk. That this must necessarily be the case is easily seen. The free surface energy $\sigma\omega$ tends to a minimum. In the case of a pure liquid σ is constant, hence only the size of the surface ω can become less. Not so in the case of a solution. Here the surface tension σ varies with the concentration c of the solution, and the possibility exists that σ tends to a minimum value on account of this variability. In order to effect this, the surface layer must be more dilute than the rest of the solution, if σ increases with increase in c. If on the contrary σ decreases as c increases, then the dissolved substance will collect in the surface layer.

Such a change of concentration in the surface layer is called *adsorption*. We speak of *positive adsorption*, when the concentration of the substance in the surface layer is greater than in the two homogeneous phases, the liquid and the gas space; and of *negative adsorption* when it is smaller.

In the deduction of the quantitative relation between adsorption and surface tension the following cases must be distinguished: Case I, the liquid is a solution, the vapour space only contains vapour of the solvent. Case II, the gas space contains, besides the vapour of the liquid, a second gas practically insoluble in the liquid. The combination of the two cases then includes most actually occurring systems.

We will first consider Case I. Let there be a dilute solution of volume V, concentration c, osmotic pressure P. Let the solution be separated from the pure solvent by a semi-permeable membrane. Let the following cycle

[1] *Helmholtz* has shown that, from *Carnot's* law, the amount of heat which is set free can be calculated when 1 gram of a liquid is transferred from a drop of radius r to a plane liquid surface. It is

$$Q_\omega = \frac{2}{\varrho_1 r} T \frac{d\sigma}{dT},$$

This amount must therefore also be the difference between the latent heat of evaporation from a curved surface and from a plane one [see *Girtler*, Ber. d. Wien. Akad. d. Wiss. **117**, II*a*, 889 (1908)].

be performed: The surface of the solution is increased by $d\omega$, whereby work $-\sigma d\omega$ is done, V remaining constant, while the osmotic pressure changes to the value

$$\left(\mathrm{P} + \frac{\delta \mathrm{P}}{\delta \omega} d\omega.\right).$$

The volume is then increased by $d\mathrm{V}$, and the work

$$+ \left(\mathrm{P} + \frac{\delta \mathrm{P}}{\delta \omega} d\omega\right) d\mathrm{V}$$

gained. Now ω must have remained constant, while σ has altered to the value

$$\sigma + \frac{\delta \sigma}{\delta \mathrm{V}} d\mathrm{V}.$$

The original surface ω is then restored, with gain of work

$$+ \left(\sigma + \frac{\delta \sigma}{\delta \mathrm{V}} d\mathrm{V}\right) d\omega.$$

Hence P also assumes its original value, and the work $-\mathrm{P}d\mathrm{V}$ must be done, in order to restore the original state. Since the cycle is isothermal, the sum of the work is zero; from which it follows that

$$\frac{\delta \sigma}{\delta \mathrm{V}} = -\frac{\delta \mathrm{P}}{\delta \omega} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This equation states that if the surface tension changes with the volume, that is to say, with the concentration, then the osmotic pressure must change with the size of the surface. This latter is only possible, however, if the concentration in the solution depends upon the size of the surface, if therefore the concentration at the surface is greater or smaller than that in the solution.

In order to recognize in what sense σ must change with V, in order that an increase or diminution of the surface concentration may occur, it is advisable to introduce the concentration c as a variable. c is, according to the above equation, a function of both V and ω. If we have n mols. in solution, c is not simply $= \frac{n}{\mathrm{V}}$; for the surface is richer or poorer, as the case may be, in dissolved substance, than if it were a part of the total liquid. If we denote this excess, reckoned per unit of surface, as a, then it is $a\omega$ for the whole surface, and this number of mols. is to be subtracted from n, in order to get the number of mols. in the solution. Hence $c = \frac{n - a\omega}{\mathrm{V}}$; it should be noted that a may be both positive and negative.

Equation (1), developed as a function of c, runs

$$\frac{\delta \sigma}{\delta c} \frac{\delta c}{\delta \mathrm{V}} = -\frac{\delta \mathrm{P}}{\delta c} \frac{\delta c}{\delta \omega}.$$

Also

$$\frac{\delta c}{\delta \mathrm{V}} = -\frac{n - a\omega}{\mathrm{V}^2}$$

and

$$\frac{\delta c}{\delta \omega} = -\frac{\mathrm{a}}{\mathrm{V}}.$$

Substituting the last two equations in the previous one, we get

$$\mathrm{a} = -c \frac{\delta \sigma}{\delta c} \frac{\delta c}{\delta \mathrm{P}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Since as a rule P increases with c, $\frac{\delta c}{\delta P}$ is positive, and it therefore follows from this equation that *if the surface tension increases with increase of concentration,* a *is negative, and the surface contains less of the solute than if it were simply a part of the liquid. If on the other hand the surface tension diminishes with increase of concentration, the solute is concentrated on the surface.*

Or, in other words, *a solute is positively adsorbed if it lowers the surface tension, and negatively if it raises it.*

If we assume that van 't Hoff's law is true for dilute solutions, then

$$\frac{\delta P}{\delta c} = RT,$$

hence

$$a = -\frac{c}{RT}\frac{\delta \sigma}{\delta c}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In the case of the surface tension of solutions, we are usually dealing with such high concentrations that we cannot regard the laws for dilute solutions as valid without further question.[1] Hence formula (3) is limited in its applications, and we are often obliged to be content with a more general formula

$$a = -f(c, T \ldots)\frac{\delta \sigma}{\delta c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which, as we have just said, $f(c, T \ldots)$ may be taken as positive.

This relation was first deduced by Gibbs [2] for the second case mentioned above on p. 46, namely, in which a gas is in contact with a liquid which does not dissolve it. It is therefore described as the Gibbs adsorption formula. Later it was given independently by J. J. Thomson.[3] The argument given above follows closely one given by Milner.[4]

At this point we may discuss how we can most usefully picture a solution to ourselves. The van 't Hoff theory of dilute solutions undoubtedly represents correctly a series of phenomena. It states that the solute is divided up like a gas down to its molecules, and that the particles thus present in the solution execute a motion which strictly agrees with the thermal motion demanded by the kinetic theory of gases. The resultant osmotic pressure, and the phenomena following therefrom, such as diffusion and many others, may thus be fully explained.

The van't Hoff theory does not tell us what these *solution-molecules* (to use a useful and frequently applied expression) really consist of. The view, which at one time was very general, that these solution-molecules are none other than the molecules of the solute, cannot be maintained; only in comparatively rare cases, such as that of a dilute solution of toluene in benzene, will this view be correct. As a rule, the solution-molecules consist of a

[1] It is only a question as to whether the *van 't Hoff* laws are valid in the interior of the solution; this does not need to be the case for the surface.

[2] Collected "Papers," Vol. I. p. 233.

[3] "Applications of Dynamics to Physics and Chemistry," p. 191. For the relation of his formula to that of Gibbs, see *F. Emslander* and *Freundlich*, Zeitschr. f. physik. Chemie, **49**, 317 (1904); also *E. Warburg* [Wied. Ann. **41**, 14 (1890)] deduced this formula.

[4] Phil. Mag. (6), **13**, 96 (1907).

compound of the molecules of the solute with those of the solvent.[1] Through the interaction between these two kinds of molecules, the internal pressure of the solution is changed, and hence at the same time all properties, such as surface tension, compressibility, and so on, which depend upon the internal pressure. Van 't Hoff's theory tells us nothing about this influence of the solute upon the internal pressure: it neglects it throughout. It is hence not surprising that the van 't Hoff theory contributes nothing directly to the explanation of the surface tension of solutions.

We can therefore distinguish from the group of properties which are comprehended in the van 't Hoff theory a second independent group, which are due to the change of the internal pressure by the solute. These properties will be described as lyotropic; the influence of the solute upon the surface tension, the compressibility, the solubility of difficultly soluble substances, and others will be called lyotropic influences. Unfortunately satisfactory methods of determining quantitatively this effect of the solute upon the internal pressure are still wanting. Hence the theory of lyotropic properties is at present, in contrast to the van 't Hoff theory, quite in its infancy.

The theory of aqueous electrolytes has been still more thoroughly transformed. That the ions are simply charged atoms or groups of atoms of the electrolyte is certainly rarely the case. Water molecules are always attached in considerable numbers to the charged ions, so that the picture of an ion, already employed by Kohlrausch, as surrounded by a mantle of water, is largely true.[2] Most ions are therefore to be regarded as fairly large solution-molecules. Hence hydration, and the lyotropic phenomena connected with it, come into great prominence in electrolytic solutions. This is especially true of the strong inorganic electrolytes; in the case of weak electrolytes with organic ions, the effects of hydration seem to be smaller and more regular. This is the reason that for them the Ostwald dilution law, which assumes only the van 't Hoff theory, and nothing concerning hydration, is valid. The departure of strong electrolytes from this law is probably only indirectly connected with the hydration. How this anomaly is to be explained is still an open question. Milner[3] and Bjerrum[4] wish entirely to transform the dissociation theory. They regard strong electrolytes as completely dissociated even at a high concentration; that an apparent decrease of dissociation sets in with increase of concentration is supposed to be due to the osmotic pressure being decreased by the electrical attraction between the ions. Ghosh[5] also assumes complete dissociation: according to him, only those ions whose kinetic energy exceeds a certain amount take part in the conduction. If his view is correct, the conditions in solutions of weakly dissociated bodies and the Ostwald law of dilution must be otherwise explained.[6]

[1] See *H. C. Jones*, "The Nature of Solution," New York, 1917. Jones and his co-workers use the term "solvate" for the loose compound between solute and solvent. A literal translation of the German "Lösungsmoleküle" has been preferred to the term "solvate molecules" which is exactly equivalent to it in almost all cases. [Trans.]

[2] See also *Born*, Zeitschr. f. Elektrochemie, **26**, 401 (1920).

[3] Phil. Mag. (6), **23**, 551 (1912); **25**, 743 (1913).

[4] Zeitschr. f. Elektrochemie, **24**, 321 (1918).

[5] Journ. Chem. Soc. **113**, 449, 707 (1918).

[6] *Ghosh*, Journ. Chem. Soc. **113**, 790 (1918). *Drucker* [Zeitschr. f. physik.Chemie, **96**, 381 (1920)] emphasizes, on the other hand, that a number of strong electrolytes (even substances such as NaCl, KCl, KBr, etc.) obey *Ostwald's* dilution law at low concentra-

Dynamic and Static Surface Tension: Velocity of Adsorption

Before we discuss the surface tension of solutions, we must deal with the question, How quickly is adsorption equilibrium reached? Obviously the final state of equilibrium is not reached in the first moment after a new surface is formed; the surface layer is of the same composition as the rest of the solution. We have a *dynamic* surface tension, and this passes over into the *static* surface tension when the adsorption is complete.

From theoretical considerations first put forward by Lenard,[1] the conclusion may be drawn that the rate of adsorption is great, and much greater in the case of negative adsorption than of positive. For in the case of negative adsorption, only a relatively small number of molecules require to be removed from the thin surface layer and passed into the mass of the liquid. It is true that the backward diffusion of the solute from the interior into the surface layer must make itself felt, for when final equilibrium is reached, this tendency to diffusion balances the force of attraction of the molecules into the interior. But this diffusion first comes seriously into operation when equilibrium is practically reached. During the first effective period of the process only the attractive forces of the molecules are at work. This part of the process, as in the case of all processes in a liquid, in which the attractions of the molecules play a direct part, proceeds very quickly. Lenard estimates the time required for the equilibrium in a cane-sugar solution (in this case a negative adsorption) to be reached up to 95 per cent. at about 10^{-8} secs.

In the case of positive adsorption, the time is also short, but sensibly longer than in the case of negative adsorption. On account of the attraction of the molecular forces, the layer of solution lying immediately below the surface, which lies within the sphere of attraction of the molecules, will rapidly become poorer in solute, since this is forced into the surface layer. If the positive adsorption is strong, this amount will not suffice; solute diffuses from the interior into the depleted layer, and is continually and rapidly taken up by the surface layer. This lasts until, just as the equilibrium is attained, the backward diffusion from the surface balances the forward diffusion. The speed depends greatly upon the absolute amount and the coefficient of diffusion of the dissolved substance. In the case of true solution, Lenard assumes periods of $\frac{1}{100}$ sec. to 1 sec. for the setting up of equilibrium up to 95 per cent.

Among the methods of measuring surface tension there are several in which the tension of a very freshly formed surface is measured, such as the methods of vibrating jets and drops: in the case of the former, for instance, the wave is formed directly at the efflux orifice, in the case of water under a head of about 2 metres in about 0·01 sec. In actual fact, the author's experiments gave, in the case of a solution of heptylic acid, which leads us to expect strong adsorption on account of its great lowering of σ, a value of $\sigma = 66$ at room temperature for a 0·005 mol. solution by the method of vibrating jets, while the purely static method of capillary rise gave for the same solution under exactly the same conditions a value 52·5; and still greater differences have been found in the case of colloidal solutions of the

tions (below 0·01 molar). He therefore rejects a fundamental change in the theory, and believes that if at higher concentrations other solution-molecules were taken into account, such as are formed by association and reaction with the molecules of the solvent, the theory would also prove correct at higher concentrations.

[1] Sitzungsber. d. Akad. Heidelberg, **5**, A (1914), 28 Abh., p. 16 *et seq.*

soaps, saponin, and other substances (see p. 534). But according to Bohr [1] inexactitudes in the physical assumptions in the case of the two methods named falsify the experimental results for fresh surfaces, so that these results are not quite certain.[2]

The method by which Hiss [3] proved the existence of a dynamic surface tension and measured the adsorption velocity appears more reliable. By means of a powerful air current, the liquid under investigation was sucked into a capillary to a height greater than that due to capillarity, and "atomized" into spray. By stopping the air current at a definite time, the liquid rapidly sank to the position demanded by surface tension. The position which the meniscus occupied at very short intervals of time after stopping the air current was now determined: Is the rate at which it falls simply equal to that of a falling liquid, or does it lag behind this value?

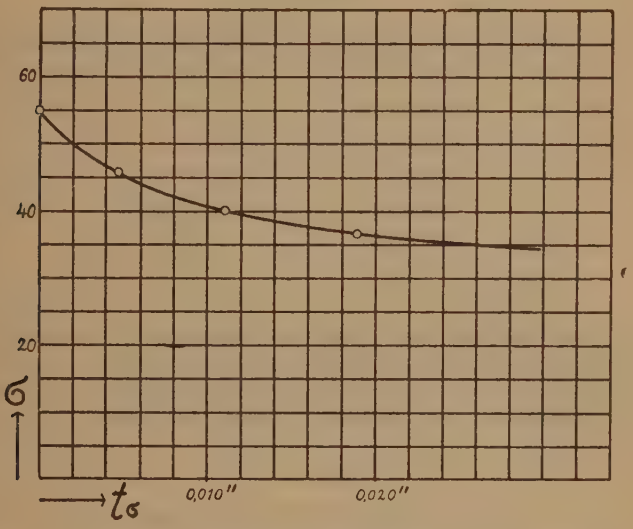


Fig. 10.—Change in the Surface Tension of an Aqueous Solution of Amyl Alcohol with Time.

If, from the distance fallen in a certain interval of time t, one calculates the theoretical time of fall t', then, after allowing for a delay t_0 due to the experimental arrangements, t and t' should be equal, provided that no lag occurred and that the surface tension was established in the shortest time measurable under the experimental conditions. This was so with pure liquids such as benzene and nitrobenzene. In each case the static surface tension was established in less than 0·001 second.

With solutions it was otherwise. There remained a difference between the time interval t and the theoretical time of fall t'. On stopping

[1] *loc. cit.* p. 24.

[2] One might suppose that the method of surface waves leads to dynamic values. This is not the case as soon as the waves have formed properly. These new molecules of the liquid do not come continually into the waves; those remain, for the most part, which were originally present.

[3] "Über die zeitliche Änderung reiner Flüssigkeitsoberflächen." Diss., Heidelberg, 1913.

the air current the meniscus remained stationary for an interval of time $t_\sigma = t - t_0 - t'$. If one calculates, according to the capillary rise formula, the surface tension corresponding with this position of the meniscus, one obtains the dynamic surface tension which obtains during the time t_σ. By choosing various initial heights for the meniscus above that of the ordinary capillary rise, a series of values for t_σ, with corresponding values for σ, are obtained. Such measurements for an aqueous solution of amyl alcohol (0·284 molar) are given in Table 12 and Fig. 10. This amounts to the measurement of an adsorption velocity. The latter is large, for the static value of the surface tension is manifestly attained in a few hundredths of a second.

Aqueous solutions of ethyl alcohol and glycerol behaved similarly.

TABLE 12

Transition from Dynamic to Static Surface Tension for an Aqueous Amyl Alcohol Solution. t = 14°

t_σ (in Seconds).	σ.
0·0000	54·9
0·0047	45·7
0·0110	40·2
0·0189	36·6
∞	34·8

The behaviour of pure water was very remarkable. In contrast to the behaviour of benzene and nitrobenzene, a lag appeared even under experimental conditions which are quite free from objection; that is to say, there was a transition from dynamic to static, as Table 13 shows.

TABLE 13

Transition from Dynamic to Static Surface Tension of Pure Water t = 16°

t_σ (in Seconds).	σ.
0·0000	81·8
0·0007	80·0
0·0040	77·2
0·0080	74·6
∞	73·8 [1]

This can only be explained by assuming that water, as an associated liquid, contains various sorts of molecules, of which one concentrates in the surface; this being the sort which would give the lowest surface tension if it alone were present in water.

It should be noted that in the Gibbs formula the static surface tension is to be inserted.

[1] The values of *Hiss* have been recalculated for dyne/cm., but a σ value of 73 for 18° has not been substituted (the 73·8 of the text should have been 73·3).

General Remarks on the Static Surface Tension of Solutions

The numerous measurements of surface tension which have been carried out upon solutions almost all relate to the surface tension against air, not against the vapour of the solvent. This is however a defect of little importance, since the values of σ for liquid—vapour and for liquid—air only differ slightly from one another (see p. 83); and this difference comes still less into question when the surface tension of dilute solutions is compared with that of the pure solvent, since then a possible influence of the air has still less effect than when liquids of quite different kinds are compared.

The surface-tension—concentration curve (shortly the σ, c curve) for mixtures of two substances will, if we take the case of no compound being formed, run a simple course between the σ's of the two substances, either linearly, or above or below the mean line, or finally with a maximum or minimum. Now we can deduce from the Gibbs adsorption law a rule, according to which a certain form of the σ, c curve should be preferred. For, according to Gibbs,[1] the rule holds *that a small quantity of a dissolved substance can lower the surface tension greatly, but cannot raise it much.* If a substance raises the tension, its concentration in the surface layer is less than in the body of the solution; if the concentration of the substance is small, the reduction therein can only be small also. In the most favourable case, pure solvent is at the surface; this would then be depleted by the small amount which is present in the surface layer, which is small compared with the total amount of liquid. If, on the other hand, the dissolved substance lowers the surface tension, and is therefore positively adsorbed, in the most favourable case the whole amount of the dissolved body might be contained in the surface. This would result on account of the small volume of the surface layer in a very noticeable change in concentration compared with the concentration in the mass of the liquid. The surface excess a, therefore, can only be small when its sign is negative; while it may be large when its sign is positive. It then follows from formula (4), p. 48, that the surface tension for small concentrations may decrease considerably, but cannot increase very much.

This produces the effect, however, that an σ, c curve running below the line connecting the two extreme σ's is more probable than one running over it. Experience also confirms this expectation. The σ, c *curves of most solutions run below the connecting line. They show a minimum or tend towards one; only a few run above the connecting line.*

The curve for benzene-toluene, for example, is a straight line.[2] Their σ's differ very little from one another.

The σ, c curves of the following run below the connecting line:

Water—fatty acids.[3]
Water—alcohols.[4]
Ether—carbon disulphide.[2]
Chloroform—carbon disulphide.[2]

[1] "Scientific Papers," Vol. I. p. 274.
[2] *Whatmough, loc. cit.* p. 22.
[3] *E. Duclaux*, Ann. de chim. et de phys. (5), **13**, 76 (1878); *I. Traube*, Ber. d. deutsch. chem. Ges. **17**, 2294 (1884); Journ. prakt. Chemie, **34**, 292 and 515 (1886); Lieb. Ann. **265**, 27 (1891); *Forch*, Wied. Ann. **68**, 801 (1899); *Whatmough, loc. cit.*; *Drucker*, Zeitschr. f. physik. Chemie, **52**, 641 (1905).
[4] *I. Traube, loc. cit.* under [3]; Journ. prakt. Chemie, **31**, 177 (1885).

Benzene—ether,[1] chloroform,[1] carbon disulphide,[1] nitrobenzene,[2] ethyl acetate,[3] and others.

Toluene—nitrobenzene [2] and others.

The following show a minimum:

Toluene—xylene.[1]

Ethyl acetate—amyl alcohol.[1]

Carbon disulphide—dichlorethylene.[1]

Acetic acid and also other fatty acids—ethyl iodide, tetrachloromethane, benzene, chloroform.[1]

Tetrachloromethane—chloroform.[1]

Benzene—ethyl iodide.[1]

A maximum for the σ, c curve occurs with

Water—sulphurit acid.[4]

The most frequent type of curve may be said to be the one in Fig. 11, convex to the axis of concentration, which falls away steeply, starting from the substance A with the higher σ, and rises slowly, starting from the substance B with the smaller σ. It is found in the case of many mixtures of organic liquids and in the case of aqueous solutions of bodies which are either weakly or not at all dissociated, such for example as the fatty acids. The drop at the A side is frequently, but not always, the steeper, the smaller the σ of the body B is; likewise, the rise at the B side is the more decided, the greater the σ of the body A. The table on next page gives examples for the numerical course of such a curve.

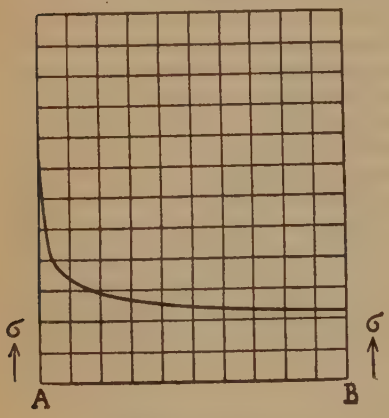


Fig. 11.—σ, c Curve.

Such a complete σ, c curve is distinguished by the fact that each of its points strives to come as near as possible to the axis of abcissæ, since σ strives to become a minimum for each concentration. The σ, c curve must therefore be a *catenary*, since also in the case of a chain stretched between two points, each point of the chain attempts to take up the lowest possible position. We do not get, or at least only in exceptional cases, the simple catenary, in which each unit of length of the chain has the same weight. On the contrary, we must imagine the different portions of the chain as loaded with different weights according to the number of different sorts of molecules present in the solutions, and the molecular forces acting between them. A theory of the σ, c curve along these lines therefore meets with serious difficulties.

[1] *Whatmough, loc. cit.* p. 22.

[2] *Ritzel, loc. cit.* p. 44.

[3] *Linebarger*, Am. Journ. Sci. (4), **2**, 226 (1896); see concerning mixtures of organic liquids, *Sutherland*, Phil. Mag. (5), **38**, 194 (1894); *Herzen*, Arch. sci. phys. et nat. (4), **14**, 232 (1902).

[4] *Röntgen* and *Schneider, loc. cit.* p. 44; *Whatmough, loc. cit.* p. 22.

TABLE 14 [1]

σ, c Curve of an Aqueous Butyric Acid Solution. $t = 25°$

c (Mol. per Litre.)	σ.
$\frac{1}{\infty}$	72·0
0·01583	70·7
0·08247	60·7
0·2675	48·3
0·4353	42·3
0·9802	33·5
2·834	28·5
9·015	27·5
11·38 (pure acid)	26·5

The general type of the σ, c curve—sharp fall at the end of the substance with the higher tension, moderate rise at the end of the substance with the lower tension—is so general, that it also appears unmistakably in cases in which we are not able to follow the whole σ, c curve, and are limited to the consideration of dilute solutions. There is a great number of substances which raise the σ of water very little, and another group which strongly depress it. Muskulus [2] already divided substances into surface-inactive and surface-active (or capillary-inactive and capillary-active), a distinction which is of course not strict, since there are enough substances which, for example, lower σ weakly; in the limiting cases, however, it is entirely correct. It is, however, more useful to speak of *surface-inactive* and *surface-active solutions*; for it is not a question of the nature of the solute alone, but also of the solvent. Only in the case of solvents with a high σ, such as water, can a strong lowering, a strong capillary-active effect, take place, while in the case of solvents with a low σ, such as ether, all substances behave as capillary-inactive; only a slight rise of σ is observed with increase in concentration of the solute.

The Surface Tension of Capillary-inactive Solutions

To the capillary-inactive solutions belong first of all those in liquids which themselves have a low σ. In the case of these, the surface tension usually rises linearly with increasing concentration of the solute, so that an equation

$$\sigma_L = \sigma_M (1 + mc) \text{ or } \Delta = \frac{\sigma_L - \sigma_M}{\sigma_M} = mc \quad . \quad . \quad . \quad (1)$$

satisfactorily represents the relation between the surface tension of the solution σ_L and that of the solvent σ_M; m is a constant. G. Jäger [3] found a behaviour of this sort in the case of solutions of benzoic acid, camphor, naphthalene, aniline, in methyl- and ethyl-alcohol, ether, acetone, chloroform, and so on. A fundamental investigation of the influence of the nature of

[1] From experiments by *Drucker*, *loc. cit.* p. 19. For the calculation see also *Freundlich*, Zeitschr. f. physik. Chemie, **57**, 427 (1907).

[2] Chem. Zentralbl. 1864, p. 922.

[3] Wien. Akad. d. Wiss. **101**, 158 (1892), and also *ibid* **100**, 493 (1891); see also *F. Schulze*, "Über die Oberflächenspannung nichtleitender Lösungen in ihrer Abhängigkeit von der Konzentration." (Diss., Rostock, 1911), who investigated various organic liquids in mutual solution; he adds a quadratic term on to the linear term, in order to represent the dependence of the surface tension upon concentration.

the solute upon the constant m is not yet available. Frequently m will be the larger, the greater the σ of the pure solute at the temperature in question would be, if it could be undercooled and kept liquid. G. Jäger states that in the case of the aromatic substances mentioned m has about the same value if the concentration be reckoned in mols. This is not surprising if we consider how little the surface tensions of related substances of high atomic weight differ from one another (see Table 5). We can easily estimate that these aromatic substances would have at the same temperatures only slightly different surface tensions; and that therefore, if we calculate the σ, c curve in a comparable manner, i.e. according to mols., m for all is practically equal.

In aqueous solution difficultly volatile non-electrolytes are surface-inactive, when they have a comparatively high melting-point and a correspondingly high σ at ordinary temperatures. The most important of these are substances rich in hydroxyl, such as sugars, glycerine, etc. Cane sugar, according to the most trustworthy measurements,[1] raises the σ of water, glycerine lowers it a little.[2]

Further, aqueous solutions of salts, especially of inorganic salts, are surface-inactive. This is quite to be expected; according to Table 4, they have sensibly higher surface tensions than water even at their melting-points, not to speak of room temperature. Here again, if we leave out secondary influences, the dependence of σ on c may be represented by a linear equation. For example, Table 15 gives the values of σ for an aqueous NaCl solution at various concentrations.

TABLE 15

Surface Tension of Aqueous NaCl Solutions [3]

$m = 0{\cdot}0228$. $t = 18°$

c (Mol. per Litre).	σ (obs.).	σ (calc.).
$\frac{1}{\infty}$	73·00	—
0·020	73·04	73·03
0·121	73·20	73·20
0·290	73·44	73·48
0·544	73·81	73·91
0·713	74·19	74·19
1·11	74·77	74·85
2·06	76·34	76·43
3·04	78·42	78·06
4·00	79·86	79·66
5·43	82·87	82·04

The calculated values differ here as in many other cases by less than 1 per cent. from the observed values.

Heydweiller [4] and his collaborators measured σ for aqueous salt solutions against pure water with great relative accuracy, and arrived, especially upon the basis of his experiments and by a comparative consideration of

[1] *Ebeling*, Sitzungsber. d. Akad. Heidelberg, A, **6** (1915), 9 Abh.
[2] *Domke*, Wiss. Abh. d. K. Normal-Eich. Komm. **3**, 41 (1902).
[3] From *Heydweiller's* measurements, Ann. d. Physik (4), **33**, 154 (1910).
[4] Ann. d. Phys. (4), **33**, 145 (1910).

the results of other workers, at the conclusion that m is not strictly constant but first passes through a minimum as the concentration increases, at a concentration of about 1 mol., and then increases again. He is probably quite right in connecting this complicated behaviour with the dissociation of the salt, and in supposing that here (to use a different expression) the lyotropic influence is superimposed upon the purely osmotic or purely electrical influence of the ions. Heydweiller expresses the dependence of m upon the concentration by means of a formula with three constants, in which he takes both the undissociated and the dissociated part of the salt into account. The constants are not sufficiently characteristic, and do not at present permit of being sufficiently definitely connected with other physical magnitudes, to be very useful here.

In comparing the action of various salts we shall at present rather regard m as constant. The behaviour of the salts may be deduced also in detail from the course of the σ, c curve (Fig. 11) and the values of σ for pure salts. The rise of the σ, c curve, and hence the value of m for a salt, is in general the greater, the greater is the surface tension of the pure salt at the temperature in question, or the greater it would be, if we could get it in an undercooled state at this temperature. On p. 42 it was stated that the surface tension of pure salts is plainly obtainable additively from the radicals composing them; and that as regards the acid radicles, a series

$$F > SO_4 > Cl > Br > NO_3 > I$$

terminated by CNS could be recognized. In the case of the alkali metals the series

$$Li > Na > K > Rb > Cs$$

is obtained. The same may be said of the m values. They are unmistakably additive,[1] and arrange themselves for the alkali metals and acid radicles in the series just mentioned, as appears from Table 16.

TABLE 16

m Values of the Alkali Salts. $t = 18°$ [2]

	SO_4.	Cl.	Br.	NO_3.
Li	—	0·0286	0·0271	0·0192
Na	0·0357	0·0228	0·0184	0·0176
K	0·0418	0·0210	0·0151	0·0158
NH_4.	0·0326	0·0195	—	0·0174

We may further add that F,[3] ClO_3,[4] CO_3[5] are close to SO_4, while I [6] and CNS [1] join NO_3 in raising the surface tension of water very little, indeed hardly at all. This entirely corresponds to the σ values for pure salts; KI and KCNS are distinguished by small σ values (see Table 4, p. 26).

[1] *Valson* [Ann. de chim. et de phys. (4), **20**, 361 (1870)] was the first to point out the additive behaviour in the effect upon the surface tension of water.

[2] Calculated from *Heydweiller's* data, *loc. cit.* p. 56.

[3] *Heydweiller, loc. cit.* p. 56.

[4] *G. Pann*, "Oberflächenspannung wässriger Sulfat-, Nitrat-, und Karbonatlösungen." Diss., Königsberg, 1906.

[5] *Röntgen* and *Schneider, loc. loc.* p. 44.

[6] *Freundlich* and *Seal*, Kolloidztschr. **11**, 257 (1912).

As regards the metallic residues, the alkali metals mostly arrange themselves in the order

$$Li > Na > K,$$

although the differences are rarely so marked as in the case of the acid radicles. NH_4 follows K, while the alkaline earth and heavy metals have higher m values than Li. This again is reflected in the σ values of the salts.

We therefore meet the same regularities in the surface tension of molten salts as in their influence upon the surface tension in aqueous solution. Since we can draw conclusions from the surface tension of pure salts regarding their internal pressure, that is, regarding their constant a in van der Waals' equation, the parallelism between the behaviour of pure salts and their behaviour in solution shows that the molecular attraction proper to the salts makes itself felt in solution as well, and appears in the lyotropic influence upon the surface tension.

The above-mentioned characteristic series

$$F > SO_4 > Cl \ . \ . \ .$$

and

$$Li > Na > K \ . \ . \ .$$

are called *lyotropic series*, and always appear again as soon as we are dealing with the non-osmotic influence of a dissolved salt. In all probability this series also corresponds to the order of hydration of the ions. In spite of numerous attempts no one has yet succeeded in determining it quantitatively, let alone in getting exact data as to its dependence upon temperature and concentration. Nevertheless, it is practically certain that with a hydrogen ion concentration such as exists in pure water, the most hydrated ions are at the sulphate and lithium ends of the lyotropic series respectively, and that the hydration decreases in the order given above. That the sodium ion is more strongly hydrated than the potassium, rubidium and cæsium ions is decisively suggested by the circumstance that the sodium salts crystallize for the most part with water of crystallization, the potassium, rubidium and cæsium salts very generally without. We are led to a similar result by a comparison of sulphates with chlorides and nitrates respectively. Among the numerical data regarding the hydration of ions we may deal first with Remy's results.[1] His assumption that the hydrogen ion attracts no water molecules is however, doubtless incorrect. According to Bohr's theory (see p. 37) a $H^{\cdot}$ ion is equal to a hydrogen atom which has lost an electron; it is, therefore, nothing but a singly charged positive nucleus. This is however so small (radius of the order of 2×10^{-13} cm.) that the $H^{\cdot}$ ion ought to have a still larger relative mobility than it already has, if it were really only a positive nucleus, and not attached to water molecules. Possibly only a few water molecules are sufficient, and the serial order of the values calculated by Remy would not be changed thereby. Remy gets these values on the basis of the following argument. Assuming that an ion moves like a sphere in a viscous liquid according to Stokes' formula—this will be discussed later (p. 344) in detail, and we shall see that its application to small spheres, as is done here, is not strictly permissible—we get too large a mobility when we ascribe to the ion its corresponding atomic radius. From the greater radius which must be postulated in order

[1] Zeitschr. f. physik. Chem. **89**, 467 (1915); but cf. the different treatment by *Born* (*loc. cit.* p. 49).

to obtain agreement with Stokes's formula—an increase which is explained by the existence of a water-mantle—the numbers in the following table are calculated. At any rate we get again the pronounced lyotropic order of the kations.[1]

TABLE 17

Degree of Hydration of Alkali Kations

Ion.	Number of Water Molecules to the Ion.
Li	<120
Na	<66
NH_4	17
K	16
Rb	14
Cs	13

Morgan and Schramm [2] have measured the surface tension of salt solutions up to very high concentrations and with strong supersaturation—a $CaCl_2$ solution, for example, up to 55·5 per cent., i.e. over 11N. The σ, c curve is here also as usual (see p. 54 and Fig. 11) decidedly convex towards the c axis, and the values of σ for supersaturated solutions join on, as we should expect, to those for unsaturated solutions.

The measurements of different observers agree in the main satisfactorily, even when the methods are very different. Among the methods used were the following:

Vibrating jets: Stocker.[3]

Vibrating drops: O. Jahnke.[4]

Surface waves: Dorsey.[5]

Capillary rise: Quincke,[6] Röntgen and Schneider,[7] Volkmann and his collaborators,[8] Heydweiller and his collaborators,[9] and others.

Maximum bubble pressure: Forch.[10]

Drop-weight: Morgan and collaborators.[11]

The greatly different values of Brümmer [12] and Loewenfeld [13] appear to be distorted by fundamental errors.

The behaviour of the acids and alkalis may also be simply deduced. Sulphuric acid and difficultly volatile alkalis, such as LiOH, NaOH, KOH, have high critical temperatures and high surface tensions at ordinary temperatures; hence they raise the σ of water. Hydrochloric acid, nitric

[1] *Remy, loc. cit.* p. 58.

[2] J. Amer. Chem. Soc. **35,** 1845 (1913).

[3] *loc. cit.* p. 13 and Zeitschr. f. physik. Chemie, **94,** 149 (1920).

[4] *loc. cit.* p. 14.

[5] Phil. Mag. (5), **44,** 134, 369 (1897); Phys. Rev. **5,** 170, 213 (1897).

[6] Pogg. Ann. **160,** 337, 560 (1877).

[7] *loc. cit.* p. 44.

[8] *loc. cit.* p. 19. See further *W. Grabowsky,* "Oberflächenspannung wässriger Chloridlösungen." Diss., Königsberg, 1904; *G. Pann, loc. cit.* p. 57.

[9] *loc. cit.* p. 56.

[10] Ann. d. Physik (4), **17,** 744 (1905).

[11] *Morgan* and *Bole,* J. Amer. Chem. Soc. **35,** 1750 (1913); *M.* and *McKirahan,* ibid. **35,** 1759 (1913); *M.* and *Schramm, loc. cit.* under [2].

[12] *loc. cit.* p. 15.

[13] *loc. cit.* p. 15.

acid, and ammonia have low critical temperatures and low surface tensions. They only influence the σ of water very little, and generally lower it. In the case of NH_3 all experiments are in favour of a lowering; in the case of HCl and HNO_3 the majority; but O. Jahnke [1] states that, using the method of vibrating drops, a lowering is only found at high concentrations, while at low ones a slight increase of σ takes place, so that the σ, c curve shows a flat minimum. A strongly marked maximum of the σ, c curve is known for aqueous sulphuric acid solutions (see p. 54 and Fig. 15a). In accordance with theory, the rise at the water side is at first only gentle. Table 18 gives a general view of the behaviour of the inorganic acids and bases; it is mainly taken from the experiments of Röntgen and Schneider.

TABLE 18

Surface Tension of Aqueous Solutions of some Acids and Bases [2]
Concentration: 1·498 mol. $t = 18°$

Substance.	σ.
Water	73·0
H_2SO_4	73·7
HCl	72·6 [3]
HBr	72·3
HNO_3	71·9
LiOH	75·5
NaOH	75·9 [4]
KOH	75·7
NH_4OH	70·0 [4]

Very remarkable is the great difference between the acids and their salts, which of course depends upon the position of the critical point. It is particularly noticeable in the case of many organic acids, above all of the fatty acids and their salts; the latter only change the σ of water very little, generally lowering it somewhat, while the acids are themselves strongly surface-active (cf. p. 61). This depends, as will be shown more fully later (cf. p. 73), upon the fact that only the undissociated acids are active, and not their ions. It may however be already mentioned here that only the salts of the lower fatty acids are surface-inactive; from about lauric acid onwards the salts as well are decidedly active, especially the stearates, oleates, etc. (see p. 645).

The same contrast is seen between the surface-active amines and their more or less inactive salts.[5] To the group of substances which, like the organic acids, lower only slightly the σ of water, belong also the organic hydroxy acids and their salts.[6]

[1] *loc. cit.* p. 14.

[2] Measurements by *Röntgen* and *Schneider, loc. cit.* p. 44.

[3] An extensive series of experiments up to high concentrations by *Volkmann* Wied. Ann. **17**, 353 (1882).

[4] Extensive series of experiments by *Domke*, Abh. d. K. Norm.-Eich.-Komm. 3 1 (1902).

[5] *Windisch* and *Dietrich*, Biochem. Zeitschr. **100**, 130 (1919).

[6] *I. Traube, loc. cit.* p. 22, further *Linebarger*, J. Amer. Chem. Soc. **20**, 12 (1898).

The great difference in the surface activity of many organic acids and bases on the one hand, and their salts on the other, permits of many applications. I. Traube and Somogyi,[1] for example, drew attention to the fact that it may be used to estimate approximately the strength of acids and bases. Thus if we add to the capillary-inactive solution of the salt of a capillary-active acid a stronger capillary-inactive acid, the acid of the salt is set free to a considerable extent, and lowers the surface tension sensibly. If the added acid, on the other hand, be distinctly weaker, little of the active acid will be driven out of the salt. so that the surface tension will be lowered not at all, or very little. It is thus possible to determine, by means of a series of inactive acids of gradated strengths at equal concentrations, approximately the strength of the acid contained in the salt. Further, the salt of a strongly surface-active acid or base may be used as indicator for titrations ; a small excess of a stronger acid or base sets the surface-active acid or base free and causes a sensible reduction in σ.[2] Windisch and Dietrich [3] have worked out and applied this method. The sodium salts of nonoic and decoic acids and eucupine bihydrochloride proved to be suitable indicators.

The behaviour of the salts in alcoholic solution is similar to that in aqueous solutions ; [4] according to Cederberg,[5] however, the linear dependence of σ upon the concentration is only valid for concentrations exceeding 0·3 N.

The Surface Tension of Capillary-active Solutions

Traube's Rule

To the capillary-active solutions belong above all the aqueous solutions of very many organic substances, the alcohols, aldehydes, fatty acids, ethers, esters, amines, terpenes, camphor, and others.[6] The σ, c curves almost always have the general form reproduced in Fig. 11. The substance with the smaller surface tension is the one which is capillary-active. It already causes in low concentration a strong lowering of the surface tension of water ; at intermediate and high concentrations, σ changes comparatively little. It mostly tends towards the value possessed by the pure organic liquid.

A theoretically well-founded formula, which gives this connexion between σ and c, does not at present exist. Its deduction, for instance, from the van der Waals theory of liquids, is no simple matter. We only need to consider that it has hardly been found possible to represent a single property of a solution—say the compressibility or density—by means of this theory. Too little is indeed known about the extent to which the attractive force acting between unlike molecules (the quantity $a_{1\,2}$ of van der Waals) must be taken into account, and the attractive forces a_1 and a_2 between like molecules ; and further, we know too little about the degree and nature of the hydration. In other words, the lyotropic pro-

[1] Internat. Zeitschr. f. phys.-chem. Biologie, **1,** 479 (1914).

[2] Upon this depends the lowering of the surface tension of solutions of alkaloidal salts by alkalis [see *Traube*, Biochem. Zeitschr. **42,** 470 (1912) ; *Berczeller* and *Csáki*, ibid. **53,** 238 (1913)].

[3] Biochem. Zeitschr. **97,** 135 (1919) ; **100,** 130 (1919) ; **101,** 82 (1919) ; **106,** 92 (1920).

[4] *Quincke*, Pogg. Ann. **160,** 565 (1877).

[5] J. Chim. Phys. **9,** 1 (1911).

[6] See especially *E. Duclaux*, *I. Traube*, *Czapek*, *loc. cit.* pp. 53 and 22 ; *Morgan* and *Neilde*, J. Amer. Chem. Soc. **35,** 1856 (1913).

perties of solutions cannot yet be expressed quantitatively, and referred to simple quantities.[1]

An empirical formula, which gives the relation between σ and c very satisfactorily, is due to v. Szyszkowski.[2] It runs thus:

$$A = \frac{\sigma_M - \sigma_L}{\sigma_M} = b \log\left(\frac{c}{c} + 1\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

σ_M and σ_L have the above-mentioned significance: b and c are constants. The following tables show that the calculated values agree well with the observed ones.

TABLE 19

Propyl Alcohol in Water.[3] $t = 15°$

$b = 0{\cdot}1973$; $c = 0{\cdot}1515$

c (Mol. per Litre)	σ (obs.).	σ (calc.).
$\frac{1}{\infty}$	73·4	—
0·03125	70·6	70·7
0·0625	68·5	68·4
0·125	65·0	64·7
0·250	59·3	59·3
9·500	51·9	52·3
1·000	43·5	44·0

TABLE 20

Isobutyric Acid in Water.[4] $t = 18°$

$b = 0{\cdot}1784$; $c = 0{\cdot}0450$

c (Mol. per Litre).	σ (obs.).	σ (calc.).
$\frac{1}{\infty}$	73·0	—
0·0187	68·6	68·5
0·0250	67·3	67·2
0·0500	63·3	63·3
0·100	57·7	57·8
0·250	48·3	48·5
0·500	40·7	40·6
1·000	32·6	32·0

Much greater deviations are found in the case of weakly capillary-active substances, such as methyl alcohol, ethyl alcohol, allylamine, in many cases

[1] *Möller* [Ann. d. Physik (4), **25,** 725 (1908); **27,** 665 (1908); Zeitschr. f. physik Chem. **65,** 226 (1908)] has attempted, starting from *Bakker's* theory (*loc. cit.* p. 11) to work out a general theory of this kind for the interfacial tension of mercury against aqueous solutions.

[2] Zeitschr. f. physik. Chemie, **64,** 385 (1908). He uses capillary rise instead of surface tension, which has no influence upon the validity of his formula, since all solutions in question have densities which differ very little from 1.

[3] Measurements of *I. Traube,* Lieb. Ann. **265,** 27 (1891).

[4] Measurements of *v. Szyszkowski, loc. cit.*

the first members of homologous series. Also in the case of the strongly surface-active higher fatty acids, the σ values calculated from the formula are lower than those observed for very dilute solutions (0·001 mol. and under).[1] Here the fact comes into play that the dissociation has not been taken into account, and that it has a sensible effect at these great dilutions, since the surface-activity is only due to the undissociated acids, and not to their ions [(cf. p. 73).

At high concentrations, 1 may be neglected as compared with $\frac{c}{c}$ in the Szyszkowski formula, and we get the equation

$$\Delta = \frac{\sigma_M - \sigma_L}{\sigma_M} = \alpha + \beta \log c \quad . \quad . \quad . \quad . \quad . \quad (2)$$

as used earlier by Milner [2] for concentrated aqueous solutions of acetic acid.

As regards the two constants of the formula, if we leave weakly capillary-active substances such as the first members of homologous series out of account, b varies in general but little from substance to substance, as may be seen from Tables 21 to 24. c, on the other hand, is a constant characteristic for every substance. It obviously represents that concentration which causes a lowering

$$\Delta_{c=c} = b \log 2 = 0{\cdot}1387,$$

that is to say, one of about 14 per cent. This constant may be called the capillary value of a substance. It is the smaller the more capillary-active the substance is. The reciprocal value $a = \frac{1}{c}$, the *specific capillary activity*, is therefore a measure of the capillary activity.

If Δ and $\log\left(\frac{c}{c}+1\right)$ are employed as co-ordinates, one obtains straight lines which pass through the origin and almost coincide.

The constants b and c may be calculated as follows. Obviously equal differences in Δ, that is, in the expression

$$\frac{\sigma_M - \sigma_L}{\sigma_M} = 1 - y,$$

correspond to equal quotients in the quantity $\left(\frac{c}{c}+1\right)$. If

$$d = \left(\frac{c_2}{c}+1\right) : \left(\frac{c_1}{c}+1\right)$$

and n is the number of differences, then

$$1 - y_n = bn \log d.$$

Hence

$$b = \frac{1 - y_n}{n \log d} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now it is easy to prove that

$$d = \frac{\frac{c_2}{c}+1}{\frac{c_1}{c}+1} = \frac{c_3 - c_2}{c_2 - c_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In order to calculate d, we must look for the c values corresponding to equal differences

[1] *I. Traube, loc. cit.* p. 62; further, *Donnan* and *Barker*, Proc. Roy. Soc., A. **85**, 557 (1911).

[2] *loc. cit.* p. 48.

in y in the y, c curve, and determine d from these values by equation (4). This value inserted in equation (3) gives $\mathfrak{b}$. In order to get $\mathfrak{c}$, we solve the equation

$$1 - y_n = \mathfrak{b} \log\left(\frac{c_n}{\mathfrak{c}} + 1\right)$$

for $\mathfrak{c}$, and substitute for

$$(e)^{\frac{1-y_n}{\mathfrak{b}}},$$

d^n according to equation (3), and take the mean of the $\mathfrak{c}$ values calculated for the various values of n.

$$\mathfrak{c} = \frac{1}{n} \sum_{n=1}^{n=n} \frac{c_n}{d^n - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If we compare the σ, c curves for the substances belonging to a homologous series, we encounter the rule emphasized by I. Traube, *that the surface activity increases strongly and regularly as we ascend the series.* Thus, in order to get the same lowering of the surface tension, we need of each successive higher member of a homologous series about one third of the concentration of the previous member, which is smaller by one CH_2 group (see Fig. 12; the concentrations are there given in mol. per litre). It is to be noted that these great differences do not depend upon the pure substances having correspondingly great differences in surface tension. On the contrary, they are very nearly equal in this respect (see Table 5).

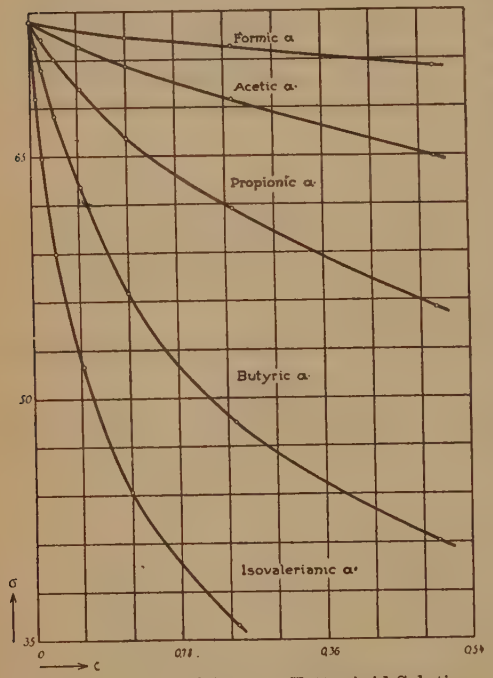


Fig. 12. σ, c Curve of Aqueous Fatty Acid Solutions.

Traube's rule may be grasped numerically with the aid of the constant $\mathfrak{c}$. If we form the quotient

$$\frac{C_n}{C_{n+1}} = \frac{O_{n+1}}{O_n}$$

for each pair of successive members of a homologous series, it is practically constant and has a value of about 3. The following tables give some examples. The capillary activity of substances of higher molecular weight is very great; in a solution of nonoic acid, which only contained 0·30 millimol per litre, and therefore only about 0·5 mg. in the 10 c.c. used for the experiment, the surface tension of water was lowered by about 25 per cent. Traces of capillary-active substances must therefore sensibly affect the σ of pure water.

TABLE 21

Traube's Rule in the case of Aqueous Solutions of the Fatty Acids

Substance.	b.	c.	o.	$\frac{o_n + 1}{o_n}$	Observer.
Formic acid . .	(0·1252)	1·38	0·73	—	I. Traube,[1] 15°
Acetic acid . . .	0·1252	0·352	2·84	3·9	,, 15°
Propionic acid . .	0·1319	0·112	8·93	3·1	,, 15°
n-Butyric acid . .	0·1792	0·051	19·6	2·2	v. Szyszkowski,[2] 18–19°
n-Valeric acid . .	0·1792	0·0146	68·5	3·5	,, 17·5°
n-Hexoic acid . .	0·1792	0·0043	233	3·4	,, 19°
n-Heptoic acid . .	0·2575	0·0018	555	2·4	Forch,[3] 18°
n-Octoic acid . .	0·3489	0·00045	2222	4·0	,, 18°
n-Nonoic acid . .	(0·2389)	0·00014	7144	3·2	,, 18°

TABLE 22

Traube's Rule in the case of Aqueous Solutions of the Alcohols and Esters

(Measurements by Traube at 15°).

Substance.	b.	c.	o.	$\frac{o_n + 1}{o_n}$
Isopropyl alcohol	0·1776	0·143	6·99	—
Isobutyl alcohol	0·2090	0·0492	20·3	2·9
Isoamyl alcohol	0·2019	0·0142	70·4	3·5
Methyl acetate	0·1571	0·185	7·43	—
Ethyl acetate	0·1643	0·0456	20·95	2·95
Propyl acetate	0·1792	0·0157	63·5	2·9

Isomeric substances, especially those of high molecular weight, have almost equal c's; they therefore lower the σ of water about equally (see Table 23).

TABLE 23

Capillary Activity of Solutions of Isomeric Substances

Substance.	b.	c.	o.	Observer and Temp.
n-Propyl alcohol . .	0·1973	0·1515	6·60	I. Traube, 15°
Isopropyl alcohol . .	0·1776	0·1426	6·99	,, 15°
n-Valeric acid . . .	0·1792	0·0146	68·5	v. Szyszkowski, 17·5°
Isovaleric acid . . .	0·1792	0·0158	63·3	,, 19°
Propyl acetate . .	0·1792	0·0157	63·7	I. Traube, 15°
Ethyl propionate . .	0·1753	0·0177	56·6	,, 15°

As regards constitutive influences, it should be noted that generally the double bond considerably lowers the capillary activity (see Table 24).

[1] *loc. cit.* p. 62. [2] *loc. cit.* p. 62. [3] *loc. cit.* p. 59.

TABLE 24

Influence of the Double Bond on Capillary Activity

(Measurements of I. Traube at 15°)

Substance.	b.	c.	o.
n-Propyl alcohol	0·1973	0·1515	6·60
Allyl alcohol	0·3514	0·618	1·62
Propyl acetate	0·1792	0·0157	63·7
Allyl acetate	0·2187	0·0417	24·0
Propyl amine	0·1459	0·0941	10·6
Allyl amine	0·4007	0·742	1·35

The parabolic equation proposed in the first edition of this book

$$\Delta = \frac{\sigma_M - \sigma_L}{\sigma_M} = sc^{\frac{1}{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

only allows the σ, c curve to be calculated with a certain degree of approximation. But it gives, when graphically represented, an instructive picture of Traube's rule, and merits mention in connexion with facts to be discussed later. s and $\frac{1}{n}$ are constants, of which $\frac{1}{n}$ (about $= 0{\cdot}7$) varies little from substance to substance, while s (the relative lowering of the surface tension for a 1 mol. solution) varies greatly from substance to substance. If we form the quotient $q = \frac{s_{n+1}}{s_n}$, Traube's rule is expressed by the fact that q is nearly constant and approximately = 2. Instead of comparing the relative lowering Δ at given concentrations, as is the case when the s values are used, we may, as in the case of Szyszkowski's formula, compare the concentrations for a given lowering Δ and form the quotient $p = \frac{c_n}{c_{n+1}}$. For the fatty acids we find p = 3·5.

Since Traube's rule has been tested in many other cases (see for example p. 229) on the homologous series of the *urethanes*, the effect of these upon the surface tension of water may be described here. There are so few measurements of this in existence, that the constants of the Szyszkowski formula cannot be accurately calculated. But since they almost all refer to a concentration of 0·1 mol., we can very well compare the q values, as the following table shows.

TABLE 25

Traube's Rule for Aqueous Solutions of the Urethanes.[1] t = 18°

Substance.	Δ (for a c = 0·1 Mol. per Litre).[2]	$q = \frac{\Delta_{n+1}}{\Delta_n}$
Methyl urethane	0·059	—
Ethyl urethane	0·106	1·8
Propyl urethane	0·185	1·75
Isobutyl urethane	0·374	2·0

[1] From experiments by *Rona* and *v. Tóth*, Biochem. Zeitschr. **64**, 293 (1914).

[2] Only in the case of ethyl urethane was the concentration 0·14 mols. per litre.

Taking logarithms the formula (6) gives us the equation for a straight line

$$\log_{10} \Delta = \log_{10} s + \frac{1}{n} \log_{10} c.$$

Fig. 13 represents the log Δ, log c curves for the aqueous fatty acid solutions; the values of c are again in mols. per litre. We see that the curves are not strictly straight, but curved concave to the log c axis. They give, however, on account of their regular parallel displacement, as we move up the homologous series, a good picture of Traube's rule.[1]

Langmuir [2] has developed the theory. The rule obviously states that while the molecular weights of a homologous series form an arithmetical progression, the specific capillary activities form a geometrical one. Hence

$$o = e^{kM}$$

where k is a constant; and for any two substances of homologous series

$$\frac{o_{n+1}}{o_n} = e^{k(M_{n+1} - M_n)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

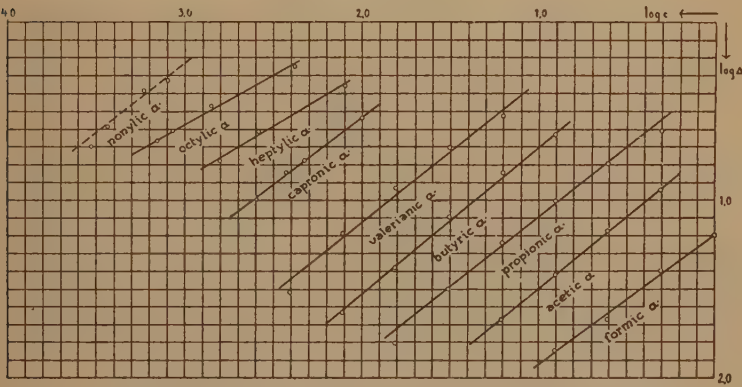


Fig. 13.—Log Δ, log c Curves of Aqueous Fatty Acid Solutions.

Langmuir considers the solutions in such dilution that the laws of van 't Hoff are valid at the surface; from the adsorption experiments on gases (cf. p. 119) it will appear that this limiting case can very well occur. That Traube's rule does not cease to be valid even at great dilutions is seen from Fig. 13. Now the work λ gained in the passage of a mol from a concentration c in the interior to the concentration at the surface is given by

$$\lambda = RT \log \frac{\varkappa a}{c}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7A)$$

Here $\varkappa$ stands for the factor of calculation which one must introduce in order to express the adsorbed amount a calculated upon 1 sq. cm. as a concentration per c.c. in the surface layer. Hence

$$\frac{a}{c} = Ke^{\frac{\lambda}{RT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

[1] *Windisch* and *Dietrich* [Biochem. Zeitschr. **97**, 135 (1919)] have tested its validity up to undecoic acid.

[2] J. Amer. Chem. Soc. **39**, 1883 et seq. (1917).

Now $\frac{a}{c}$ is proportional to o. In order to see that this is the case, we substitute in the Gibbs adsorption formula (cf. p. 48)

$$\frac{a}{c} = -\frac{1}{RT}\frac{d\sigma}{dc}$$

the value of $\frac{d\sigma}{dc}$. Equation (1), p. 62, gives

$$-\frac{d\sigma}{dc} = \frac{b\sigma_M}{c+c}.$$

For small concentrations we can neglect c as compared with c; hence

$$\frac{a}{c} = \frac{b\sigma_M}{RT}\cdot\frac{1}{c} = \frac{b\sigma_M}{RT}\cdot o$$

When this is substituted in equation (8) and the constants are united to a new constant K′, we get

$$o = K' e^{\frac{\lambda}{RT}}$$

and for two members of a homologous series

$$\frac{o_{n+1}}{o_n} = e^{\frac{1}{RT}(\lambda_{n+1}-\lambda_n)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

From equations (7) and (9) it follows that

$$\Delta = \lambda_{n+1} - \lambda_n = RTk(M_{n+1} - M_n). \quad . \quad . \quad . \quad . \quad (10)$$

Traube's rule therefore states that *between any two successive members of a homologous series there exists a constant difference in the work which is necessary in order to bring a mol of the capillary-active substance from the surface into the solution, and this work increases by a constant amount as the molecular weight increases.* A simple relation of this kind is comprehensible, when no sensible differences in the hydration exist, and further, if each additional CH_2 group comes into play in the same manner as each previous one. This is only conceivable, if they are all situated in the same way on the surface, that is, the CH_2 chains must be spread out completely in the surface; and this must also remain true for higher concentrations than are assumed in Langmuir's argument, since Traube's rule is fulfilled at fairly high concentrations.

The value of Δ amounts to 700 gram-calories in round figures, if we put

$$\frac{o_{n+1}}{o_n} = 3{\cdot}4$$

in accordance with the most trustworthy values in Tables 21 and 22, calculate from this the constant $k = 0{\cdot}08732$ in equation (7), and substitute this value in equation (10).

By means of an argument similar to that on p. 67, Langmuir [1] arrives at an equation

$$\lambda = \lambda_0 + \Delta n. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

for each group of substances belonging to a homologous series; here n is the number of CH_2 groups, λ_0 a constant which is characteristic of each group of substances. It is large and positive for the substances with strong capillary activity, such as the tertiary alcohols, primary amines and alco-

[1] J. Amer. Chem. Soc. **39**, 1891 (1917).

hols, esters, fatty acids, etc. It decreases and becomes negative when we pass to less active substances, such as the amides and dibasic acids. Table 26 gives the values of λ_0 calculated by Langmuir; they are calculated for a slightly smaller value of A (625 instead of 700).

TABLE 26

Surface Work λ_0 for various Groups of Capillary-active Substances

Group.	λ_0 (in gm. calories).
Tertiary alcohols	+ 950
Primary amines	+ 600
Primary alcohols	+ 575
Esters	+ 470
Monobasic acids	+ 473
Ketones	+ 295
Aldehydes	+ 210
Amides	— 510
Dibasic acids	— 700

We might be surprised that Traube's rule does not appear in the case of the *pure* organic liquids; their surface tension is nearly equal (see Table 5). Langmuir [1] and Harkins [2] explain this as follows. Liquids, the molecules of which have much residual affinity, have a high surface tension; such as are to a great extent saturated, a small one. The reason for this is that at the limits of the liquid the residual valencies, which cause the internal pressure in the interior, project into the vapour space in a manner similar to that which will be discussed in detail later in the case of solids (cf. p. 122); according as these projecting valency forces are large or small, the potential energy of the surface, that is to say the surface tension, is likewise large or small. In the case of liquids such as the organic substances, the molecules of which contain along with unsaturated groups (such as COO-, CO-, or a double bond) a considerable number of saturated groups, such as the CH_3 group, the molecules will take up such a position on the surface that the CH_3 group is directed outwards, since this makes the surface tension a minimum. In pure liquids, consequently, in contrast with the dilute aqueous solutions of the same substances, the molecules will set themselves at right-angles to the surface, with the CH_3 groups outwards; hence the almost equal value of σ in the case of pure substances. In dilute solutions, on the other hand, the molecules lie, as just explained, with the whole length of their chains in the surface, and the work λ and the tension σ change correspondingly strongly with the length of the chain.

In the case of the inorganic salts, on the other hand, a parallelism appears between the behaviour of the molten salts and their aqueous solutions. We may draw the conclusion that with them there are no such differences in the position taken up by the molecules, and that the strength of the residual valencies takes effect both in the case of the molten salts and in the case of their solutions.

It is clear that a relation must exist between the capillary activity of

[1] Met. chem. Eng. **15**, 469 (1916); J. Amer. Chem. Soc. **39**, 1848 (1917).

[2] *Harkins, E. C. H. Davies,* and *G. L. Clark,* ibid. **39**, 354, 541 (1917); *Harkins* and *H. H. King,* ibid. **41**, 970 (1919); *Harkins, G. L. Clark,* and *Roberts,* ibid. **42**, 700 (1920).

aqueous solutions of these substances and their *tendency to dissolve* [1] in water. If λ is large, if it requires much work to bring the substance from the surface into the interior, then it is very active and will be difficultly soluble ; in the case of a small λ the substance is less active and more soluble. As the surface activity rises in homologous series, the tendency to solution as shown by the solubility sinks, although not with the same comparatively strict regularity of Traube's rule, but nevertheless in so far similarly, in that the solubility decreases several-fold from member to member. The relation between surface activity and tendency to dissolve also appears in the fact that the unsaturated compounds are more soluble in water in accordance with their smaller surface activity. That the regularity is less sharply defined in the case of solubility arises from the fact that, in comparing the capillary activity, dilute solutions are considered, whereas in comparing solubilities we get into the region of concentrated solutions.

The marked lowering of the surface tension of water by small amounts of active substances makes itself evident in many phenomena, and has many applications. Thus the lively motion produced in a water surface by contact with ether vapour depends upon it ; the lowering of σ does not proceed equally strongly at each part of the surface, and so liquid is drawn from a place with lower tension to one with higher. The same local differences in σ cause the lively motion which pieces of camphor exhibit upon a pure water surface. That the lowering of σ by camphor vapour, and not capillary-electrical processes, is responsible, is seen from the fact that a direct contact of the camphor with the water is not necessary ; the motion also appears when the piece of camphor lies upon a light slip of mica.[2] Similar motions are shown by granules of many surface-active and volatile substances, such as benzoic acid, atropine, crushed flowers and leaves which contain volatile oils (flowers of camomile, leaves of mint and rosemary, etc.),[3] and also by granules of silver and barium propionates and butyrates, etc.,[4] in the case of which small amounts of hydrolytically separated fatty acids suffice to bring about strong local differences in surface tension.

Also, the so-called " tears " of strongly alcoholic wines are a consequence of the strong variation of σ with concentration.[5] The upper part of the glass, which is not completely filled with wine, is only wetted by the liquid. This wetting layer is subjected, on account of its large surface, to rapid evaporation, and the alcohol particularly escapes from it. Hence there remains behind a liquid poorer in alcohol and having a higher surface tension. On account of the high tension, this layer contracts into drops, which run like tears down the walls of the glass, while neighbouring points of the wall are again wetted by fresh liquid, which comes from the bulk of the wine.

[1] It is more correct to use this more general expression than the expression " solubility." For the concept " solubility " refers to an equilibrium in presence of the solid substance, while here more generally we are speaking of the tendency of the substance to enter into a phase ; a tendency which also is shown (without the presence of solid substance) in the distribution between two phases. The word " soluble " may, however, be used in this general sense.

[2] *Tomlinson*, Chem. News, **52**, 50 (1885).

[3] *Liégeois*, Arch. d. Physiol. **1**, 35, 236 (1868).

[4] *Lescœur*, Bull. Soc. Chim. (2), **24**, 270 (1876). See also *Gattermann* [Ber. d. deutsch. chem. Ges. **18**, 1484 (1885) concerning the corresponding behaviour of small crystals of aromatic diamines.

[5] *J. Thomson*, British Assoc. Rep. 1855. Rep. 2, p. 16.

Both in technology and in the laboratory, the surface tension of solutions of active substances is used to determine their content. For this purpose the stalagmometer is frequently employed, which permits of quick and convenient determinations by the drop-weight method.

If it is desired to free a contaminated surface or a solution from a capillary-active substance, the surface may be brushed repeatedly with filter paper (according to Nansen [1] and Frl. Pockels [2]) or the solution may be filtered through charcoal. In the case of the latter process particular note must be taken of the fact that other dissolved substances may also be removed, and the concentration thus be altered.

It is frequently desired to change the surface in a known manner with respect to its content of active material. Frl. A. Pockels [3] makes use of the following arrangement. The liquid is made to fill a rectangular glass or metal trough to the brim, and the surface is divided by well-fitting movable strips of glass. These must project sufficiently far from the liquid surface, and be entirely unwettable at the upper part. If we now contaminate the surface on one side of a strip of glass, say with a difficultly soluble fatty acid, the contaminated part of the surface can, by moving the strip of glass, be made larger or smaller as desired, and the fatty acid in the surface layer concentrated or diluted. The boundary of the contaminated layer is recognized by the fact that pure carbon or talc powder, previously dusted on the pure liquid, is forced back by the oil-layer (p. 312). This method was further developed by Devaux [4] and Langmuir.[5]

In order to produce as fresh and clean a surface as possible, the Röntgen [6] double funnel is used, in which the liquid rises up in an inner funnel, overflows over its rim, and flows into an outer concentric funnel.

The Surface Tension of Solutions of several Substances

As regards solutions of more than one substance, investigations by Rother,[7] and also by Whatmough,[8] on the surface-inactive solutions of inorganic salts in water are available. In view of the slight influence exerted by salts on the tension of the water, it is not surprising that a formula deduced from the rule of mixtures sufficiently reproduces the observed results. If therefore $\sigma_{1\,2}$ is the surface tension of the mixed solution, and σ_1 and σ_2 are those of the solutions before mixture, then

$$\sigma_{1\,2} = n_1\sigma_1 + n_2\sigma_2$$

reproduces the relation, where n_1 and n_2 are the fractions of the two solutions entering into the mixture, that is, the ratios of the separate volumes to the final total volume. The sum of the two is naturally always equal to unity.

But according to the experiments of v. Szyszkowski, the rule of mixtures may also be applied to a large extent, under definite circumstances, to the surface-active solutions. This is the case when we consider *capillary-equivalent* solutions. Those solutions are capillary-equivalent which produce the same lowering of the surface tension. If we consider the aqueous solutions of the fatty acids, then according to p. 62, those solu-

[1] Norwegian N. Pole Exped. Sci. Papers, Part 10 (1900).
[2] Nature, **43**, 437 (1891); **46**, 418 (1892); **48**, 152 (1893); **50**, 223 (1894); Die Naturwissenschaften, **5**, 137, 149 (1917).
[3] *loc. cit.* p. 62.
[4] Journ. de Phys. (4), **3**, 450 (1904); (5), **2**, 699, 891 (1912); Rep. of the Smithsonian Inst. 1913, p. 261.
[5] J. Amer. Chem. Soc. **39**, 1869 et seq. (1917). [6] Wied. Ann. **46**, 152 (1892).
[7] Wied. Ann. **21**, 576 (1884). [8] *loc. cit.* p. 22.

tions of two successive members of a homologous series are capillary-equivalent for which the relation

$$c_1 = \frac{c_1}{c_2} c_2 = hc_2$$

holds. The suffixes 1 and 2 refer to the lower and higher of the two acids respectively. If we have a mixture of any two—not capillary-equivalent—solutions, the concentrations of which were originally c_1' and c_2', then the lowering of the surface tension in the mixed solution is the same as if it were produced by a concentration $c_{1\,2}$ of acid 1, for which the relation

$$c_{1\,2} = n_1 c_1' + n_2 h c_2'$$

holds; n_1 and n_2 are again the fractional components. It follows from this relation that if the original solutions were capillary-equivalent, if therefore $c_1' = hc_2'$, the equation just named gives $c_{1\,2} = c_1'$; that is, the concentration in the mixture acts like that of the original solution; the surface tension of the mixture is therefore equal to that of the original solutions. Hence we have the law: *Two solutions of equal surface tension, when mixed in any proportion, give solutions of the same surface tension as the original solutions*; a law which v. Szyszkowski was able to confirm.

The rules just given must be limited in their application in so far as they are only strictly valid, when the substances in question follow exactly the same capillary law of dilution; the b values must be equal. This is, however, as Tables 21–24, pp. 65-6, show, not always the case; we then get occasionally corresponding departures from the simple behaviour. If the concentrations are different, the possibility must be reckoned with of one active substance displacing the other from the surface. The experiments [1] hitherto made, which are not very exhaustive, suggest that this is the case.

Mixtures of active and inactive substances deserve special attention. Experiments in this direction are due particularly to Worley [2] and Berczeller.[3] Worley measured the surface tension of an aqueous solution of aniline, containing increasing amounts of common salt. Although NaCl alone raises the σ of water (see Table 15, p. 56), the addition of it lowers σ considerably in the case of the aniline solution, as Table 27 shows.

TABLE 27

Effect of NaCl on the Surface Tension of Aqueous Solutions of Aniline Strength of Aniline Solution, 0·183 mol. per litre. t = 20°

Concentration of NaCl Solution (Mol. per Litre).	σ.
$\frac{1}{\infty}$	54·8
0·6836	51·8
1·367	49·6
2·051	47·8
2·894	45·9
3·418	45·8

[1] *Berczeller*, Kolloidzeitschr. **23**, 31 (1918).
[2] Journ. Chem. Soc., **105**, 263–264 (1914).
[3] Biochem. Zeitschr. **66**, 173 (1914).

Here again capillary activity and tendency to solution are antibatic to one another; the NaCl lowers the solubility of aniline, and raises correspondingly the capillary activity of its solution, since it now takes more work to bring aniline from the surface into the interior of the solution. Berczeller arrived at the same result by measurements on capillary-active substances such as phenol, α-naphthol, thymol, in solutions which contained NaCl, KCl, NH_4Cl, or K_2SO_4.

Berczeller further draws attention to the fact that in saturated solutions of substances such as menthol, phenol, or camphor, the surface tension remains practically the same, even when we dissolve salt in the water; the lowering of σ just described is not observed, probably because the concentration of the active material at the surface cannot be further increased by the presence of the salt. In saturated salt solutions, e.g. those of $(NH_4)_2SO_4$, the solubility of these capillary-active, difficultly soluble substances becomes, as Berczeller shows, so small that the surface tension is no longer altered, even when the substances named are warmed in the salt solution.

In the case of the influence just described of electrolytes upon the surface tension of capillary-active substances, we are dealing with a lyotropic influence of the salt, such as it exerts upon the solubility of difficultly soluble substances, etc. (cf. p. 78). It is only perceptible, as is generally the case with these lyotropic influences, at higher concentrations. Now, according to Windisch and Ph. Osswald,[1] the surface tension of solutions of fatty acids is affected by acids even when fairly dilute, which is unmistakably due to a change in the dissociation of the fatty acid. While the σ of an aqueous octyl alcohol solution is only as much affected by the addition of dilute HCl or NaOH solution as it would be by addition of an equal volume of water, an addition of an equally concentrated solution of HCl to a nonoic acid solution causes a sensible fall in surface tension; that the addition of NaOH raises it is comprehensible, since the resulting salt is much less active than the acid. If we add acids of various strengths to the nonoic acid solution, the lowering of the surface tension runs parallel with the strength of the acid added; the effect may be calculated numerically upon the supposition that, compared with the surface activity of the non-dissociated nonoic acid, the activity of the H′ ion and of the nonoate ion may be neglected. Hence a given concentration of acetic acid produces the same lowering of σ as one of formic acid or hydrochloric acid which would produce the same amount of undissociated nonoic acid according to the law of mass action. Corresponding to the reduction of the dissociation of nonoic acid, the σ of a nonoic acid solution is also lowered by addition of sodium nonoate; an observation already made earlier by v. Szyszkowski,[2] namely, that the σ of a solution of isovaleric acid is more strongly lowered by the addition of its own weakly active barium salt, than would correspond to the sum of the separate effects. The slight lowering of σ for water in pure solutions of the fatty acid salts is referred by Windisch and Ph. Osswald to a hydrolytic splitting-off of fatty acid.

Upon the basis of these experimental results the assumption will be made quite generally in the following pages that also at other boundary surfaces only the non-dissociated fatty acids (or non-dissociated amines) are sensibly adsorbed, but not their ions. On this account dissociation ought

[1] According to unpublished researches; see also *Windisch* and *Dietrich*, Kolloidzeitschr. **26**, 193 (1920).

[2] *loc. cit.* p. 62.

to have been taken into account in comparing the capillary activity of the fatty acids (cf. p. 65). But the dissociation constant has not been measured for those members of the series which were of chief interest.

The Experimental Proof of Gibbs's Adsorption Law

In capillary-active solutions the reduction of the surface tension with the concentration is so great that we should expect a sensible positive adsorption. The absolute amounts adsorbed remain, however, small. For example, for a solution of the strongly active nonoic acid, we should calculate according to the Gibbs formula (see p. 48) at a concentration of 0·0005 mol. per litre an adsorbed quantity of about 1×10^{-9} mol. per square centimetre, or about $1{\cdot}5 \times 10^{-7}$ grams. We should have therefore to produce a very large surface in a very small solution if we wished to detect a change in concentration caused by adsorption in the surface layer (chiefly contained in the foam) or in the remaining liquid. To get a large surface remains, however, for the interface liquid—gas a difficult problem. The easy relative mobility of the liquid particles leads to a rapid production of the minimum surface, and renders difficult any observation of the adsorption.

Nevertheless, Miss Benson [1] early succeeded in proving that in the case of an aqueous amyl alcohol solution, which froths strongly, the separated froth has a higher content of amyl alcohol than the original solution (0·0394 mol. against 0·0375 mol.). The surface excess is positive, as theory demands for a substance so strongly active as amyl alcohol in aqueous solution.

Donnan and Barker [2] carried out semi-quantitative experiments. They allowed a considerable volume of air to rise in fine bubbles through a long column, which was filled with an aqueous nonoic acid solution. The liquid column was divided in a manner similar to a fractional distillation column, by means of inset pieces of tube, into a number of divisions, through which the bubbles slowly passed. By this means the changes in concentration were as far as possible limited to the lower divisions of the column, and the adsorbed material given up at the top by the bubbles as they re-united, did not disturb the effect by diffusing downwards. The content of the solution in the various divisions was determined by drop-counting measurements, a method which, on account of the great variation in the σ of the solution with concentration, is entirely to be recommended. It was of course expressly determined that the loss by evaporation of nonoic acid only accounted for a small fraction of the change of concentration actually observed.

The results of the measurements are given in the following table. Under c stands simply the initial concentration of the nonoic acid, which may be regarded as equilibrium concentration, since the change produced by adsorption only amounts to fractions of 1 per cent; a (calc.) is the amount condensed on the boundary surface as calculated from the Gibbs adsorption formula. a (obs.) and a (calc.) agree so far that we may say that the Gibbs formula is fulfilled as regards the order of magnitude. We cannot conclude definitely from these results in what way the adsorbed amount depends

[1] J. physic. Chem. **7**, 532 (1903). Less certain are measurements of *Zawidski* [Z. physik. Chemie, **35**, 77 (1900); **42**, 612 (1903)], who made similar experiments with aqueous solutions of hydrochloric and acetic acids. As these do not froth alone, he added some saponin, which produces a strong froth. This procedure is scarcely unobjectionable. The surface excess was positive.

[2] *loc. cit.* p. 63.

upon the concentration in the solution, so that this question will not be discussed until a later stage (cf. p. 172).

TABLE 28

Adsorption of Nonoic Acid at the Interface Water—Air. $t = 16{\cdot}5°$

c in Millimol. per Litre.	a (obs.) Micromol.[1] per sq. cm.	a (calc.)[2] according to Measurements of σ by Donnan and Barker at 16·5°.	a (calc.) according to Measurements of σ by Forch [3] at 18°.
0·154	0·00060	0·00035	0·00037
0·316	0·00096	0·00072	0·00078
0·480	0·00069	0·00080	0·00100
0·509	0·00058	—	0·00103

The theory requires a negative adsorption for aqueous solutions of the inorganic salts; the surface layer must therefore consist of a more dilute solution or of pure water, a consequence already deduced by E. Warburg.[4] This has not yet been proved experimentally. According to Lenard,[5] however, the fact that during evaporation no electric charges or charged ions enter the gas space speaks in favour of it. It appears to me difficult to reconcile with this the fact that the surface tension of salt solutions does not remain practically unaltered, but actually increases distinctly.[6]

The Influence of Temperature upon the Surface Tension of Solutions

By the term solutions we shall here naturally understand all liquids containing more than one kind of molecule, in particular also associated liquids. In the case of the influence of temperature upon the surface tension of a solution the distinction must be made as to whether the equilibrium between the different kinds of molecules contained in the solution changes greatly with temperature or not. For example, we must reckon with a large displacement, when the solubility of the dissolved substance changes considerably with change of temperature, while the displacement is in general small when the solubility is but little affected by temperature. If no, or only a small, displacement of equilibrium takes place, then the dependence of σ upon temperature in the case of liquids which contain only one kind of molecule is similar; here also, for a solution of given concentration, an equation

$$\sigma_t = \sigma_0[1 - \gamma(t - t_0)]$$

suffices. Since the values of γ for different liquids, particularly in the case of those which are completely mutually miscible, are not very different (see Table 6), the γ, c curves are, as we should expect, linear or slightly

[1] Micromol. = millionth of a mol.

[2] The dissociation of the nonoic acid is not taken into account.

[3] *loc. cit.* p. 59. The experiments are given here because they allow of the calculation of a even at the highest concentration.

[4] Wied. Ann. **41**, 14 (1890).

[5] Sitzungsber. d. Akad. Heidelberg, **5**, A (1914), 29 Abh. p. 19.

[6] For reasons in favour of a positive adsorption in extremely dilute salt solutions, see p. 279.

bent between the end-values for the pure liquids. We thus get, when we compare the σ, c curves for various temperatures, a series of lines which differ very little from one another. In a normal $NaNO_3$ solution, for example, γ has a value of 0·0016 as compared with 0·002 for pure water.[1]

Of surface-active solutions, according to Worley,[2] the solution of isobutyl alcohol in water belongs to this group; σ falls at different concentrations with the temperature, and the value of γ changes but little.

To apply Eötvös' considerations to these solutions is in principle not free from objection, since on account of the adsorption the composition of the surface layer is different from that of the solution in bulk. Nevertheless, in the case of liquids with a small σ the adsorption is of so little importance on account of the smallness of $\frac{d\sigma}{dc}$ that it cannot surprise us if the above-named rule is valid to a large extent. Thus Ramsay and Aston,[3] and Pekár,[4] found that we get for mixtures of normal organic liquids the same temperature coefficient $k = 2{\cdot}1$ for the molecular surface energy, if we introduce as molecular weight of the solution the mean molecular weight; thus

$$M_{Solution} = \frac{n_A M_A + n_B M_B}{n_A + n_B}$$

where M_A and M_B are the molecular weights of the components of the liquid, and n_A and n_B the number of molecules. With a certain amount of caution it is permissible, in the case of solutions of two liquids of small σ such as aniline-phenol, aniline-nitrophenol, etc., to conclude from departures from this simple additive behaviour that compounds exist.[5]

In the case of solutions, in which the equilibrium between the different kinds of molecules is strongly displaced by temperature change, we must reckon with a much more complex behaviour of the σ, t curves. Thus solutions of aniline and of phenol in water are strikingly different in their behaviour from the above-mentioned solution of isobutyl alcohol in water. In the case of the former pair the solubility in water rapidly increases with increase of temperature; in the case of aniline from 0·333 mol. per litre at 20° to 0·773 mol. per litre at 100°; in the case of phenol from 0·893 mol. per litre at 20° to 3·82 mol. per litre at 68·8°; while in the case of isobutyl alcohol the solubility only changes from 1·215 mol. per litre at 20° to 1·08 mol. per litre at 100°. Worley [6] found in the case of dilute aniline solutions a fall of σ with rise of temperature; in the case of concentrated ones, on the other hand (over 0·215 mol.), an increase in σ with temperature. In the case of phenol he likewise observed with more dilute solutions a sinking of σ

[1] According to the measurements of *Pann*, *loc. cit.* p. 57.

[2] Journ. Chem. Soc., **105**, 260 (1914).

[3] Zeitschr. physik. Chemie, **15**, 89 (1894): Proc. Roy. Soc. **56**, 182 (1894); see also *Padoa* and *Manteucci*, Atti R. Accad. d. Lincei (5), **23**, II. 590 (1915).

[4] Zeitschr. f. physik. Chemie, **39**, 433 (1902).

[5] *Kremann* and *R. Ehrlich*, Wien. Monatshefte, **28**, 863 (1907); *K.* and *E. Philippi*, ibid. **29**, 891 (1908). How quite generally the presence of compounds can make itself felt in testing the *Eötvös* rule is shown by experiments of Mlle. *Przykuska* [J. Chim. Phys. **7**, 511 (1911)]; if we measure the σ of vacuum-distilled diphenylamine *in vacuo*, we get a normal k: if the distillation has been carried out in air, we get a smaller value for k, even when σ is determined *in vacuo*.

[6] Journ. Chem. Soc., **105**, 264 et seq. (1914).

with temperature, with higher concentrations (over 0·35 mol. per litre) σ goes through a minimum (at 40–50°) to rise again at higher temperatures.[1] This is quite intelligible : greater solubility means great affinity between the dissolved substance and water, and hence less tendency to drive it out of the interior of the liquid ; hence smaller capillary activity, higher surface tension.

In the case of associated liquids, we meet further examples of unusual σ, t curves of this sort. Such a case is liquid sulphur ; it is indeed in many respects the prototype of a liquid, in which complicated chemical equilibria are present. According to Zickendraht [2] the σ of sulphur sinks from the melting-point 114·5 [3] only very slightly to 59 dyne-cm. at 160°, then rises to 118 at 250°, sinks again to 59 at 300°, to fall still further to about 44 at the boiling-point (444·5°). The σ, t curve has therefore a pronounced maximum, as must also occur in the above-mentioned solutions of aniline and phenol in water at higher temperatures. Since the equilibria between the different sulphur molecules do not by any means adjust themselves easily, but depend [4] to a great degree upon the presence of foreign substances, it is entirely comprehensible that the results of different observers [5] vary greatly from one another, and that observations with rising or falling temperature, after longer or shorter boiling, in presence of catalysts such as NH_3, SO_2, etc., give quite different σ values. But obviously the form of sulphur which occurs at higher temperatures has a high surface tension. Further, the other interfacial tensions also change with temperature, and correspondingly the tendency to wetting. According to Rudge [6] sulphur wets glass badly from the melting-point to about 160°, while it wets it increasingly better above this temperature. Zickendraht suitably chose for the measurement of σ a method (bubble-pressure) as far as possible independent of the contact-angle. Similar phenomena—anomalous temperature coefficient, dependence of σ upon the previous treatment—were found by Walden and Swinne [7] for methylene cyanide.

In the case of water, the temperature coefficient is not distinguished by such striking peculiarities, but the circumstance that it is not symbatic to the coefficient of expansion, as is the case with other liquids (cf. p. 31), is connected with the association, and is probably to be explained as follows. The surface-layer consists fairly uniformly from 0° to high temperatures chiefly of those molecules which, if they alone made up the liquid, would give the smaller surface tension ; probably, therefore, of those of smaller molecular weight (cf. also p. 52). In the interior of the water, on the other hand, the displacements of the equilibrium cause the anomalies in density.

The Eötvös argument can hardly ever be applied to associated liquids and their solutions. It will not do to conclude from a comparison of the departures from Eötvös' rule in the case of water and aqueous salt solutions, that the degree of association in salt solutions scarcely differs from

[1] Obviously in these cases the σ, t curve must exhibit a maximum, for at the critical point the surface tension must again become zero.

[2] Ann. d. Physik. (4), **21**, 141 (1906).

[3] Natural solidification-point of monoclinic sulphur.

[4] See *A. Smith* and *W. B. Holmes*, Zeitschr. f. physik. Chemie, **54**, 257 (1906) ; *Hoffmann* and *Rothe*, Zeitschr. f. physik. Chemie, **55**, 117 (1906).

[5] See particularly *Capelle*, Bull. Soc. Chim. (4), **3**, 764 (1908) ; *Rudge*, Proc. Cambridge Phil. Soc. **16**, 55 (1911).

[6] *loc. cit.* under [5].

[7] Zeitschr. f. physik. Chemie, **79**, 717 (1912).

that in pure water.[1] The similarity of the departures is rather to be interpreted in the sense that in the case of the salt solutions, as well as in pure water, the surface-layer consists of the more capillary-active molecules above referred to.

Only in rare cases does Eötvös' rule allow of a conclusion being drawn as to whether, in a tautomeric liquid, both kinds of molecule are present, or only one. Let one kind of molecule be A, the other B; if now we have reason to suppose that the simple liquids are normal and obey Eötvös' rule, and if their critical points are sufficiently different from one another, the temperature curves of the free surface energy would be two parallel straight lines for the two liquids (see Fig. 14). The lower one belongs to the substance with the lower critical temperature, the upper one to the one with the higher. If the liquid consists at higher temperatures mainly of A, at lower of B, then we have the two portions of curves EF and CD; for an intermediate temperature, at which the two kinds of molecules are present, we have the bent piece of the curve DE. While therefore at higher and lower temperatures k has the normal value about 2·1, it passes through a maximum at an intermediate temperature. From a behaviour of this sort we could infer the presence of both kinds of molecules in a tautomeric liquid. Schenck and Ellenberger,[2] who were the first to put these considerations forward, actually found such a relation between the k value and temperature in the case of dibenzoylacetone and acetylacetone, and Walden and Swinne[3] in the case of ethyl cinnamate. The method appears, however, not to be very fruitful, since evidently many conditions must be fulfilled which do not appear very frequently together.

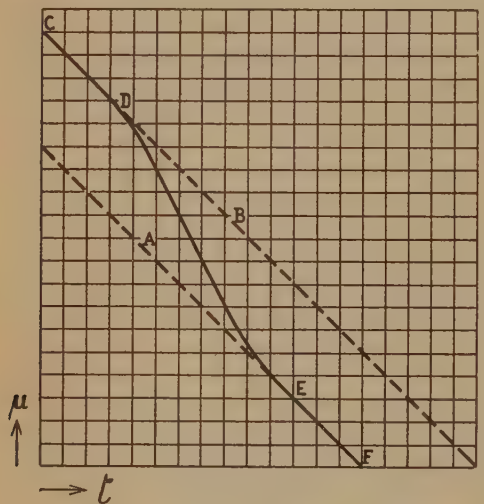


Fig. 14.—μ, t Curves of Tautomeric Substances.

The Relations of the Surface Tension of Solutions to their other Properties

The same properties, with which the surface tension of pure liquids is connected, are related to it also in solution.

The compressibility and power to dissolve of difficultly soluble substances ought therefore to be antibatic to the surface tension. This is indeed often the case. For salt solutions, Röntgen and Schneider[4] and Geffcken[5] in particular drew attention to this fact. In the case of a series

[1] *Zemplén*, Ann. d. Physik (4), **20**, 783 (1906) and **22**, 391 (1907); see also *Padoa* and *Tabellini*, Atti R. Accad. d. Lincei (5), **23**, I. 88 (1914).
[2] Ber. d. deutsch. chem. Ges., **37**, 3443 (1904).
[3] Zeitschr. f. physik. Chemie, **79**, 732 (1912).
[4] *loc. cit.* p. 44.
[5] *loc. cit.* p. 44.

of mixtures of organic liquids, Skirrow,[1] Christoff,[2] and Ritzel [3] pointed out this connexion. It frequently fails, however,[4] and in particular the compressibility and solubility curves by no means always lie above the line joining the values for the pure liquids, if the curve of surface tensions runs below it. It is therefore true rather for capillary-inactive solutions, seldom or never for capillary-active ones.

The agreement sometimes becomes better if we do not use the true coefficients of compressibility

$$\beta = -\frac{1}{v}\frac{dv}{dp},$$

but instead a derived quantity used by Röntgen and Schneider, the *relative molar compressibility*. In the case of ordinary compressibilities the changes of volume occurring for like changes of pressure referred to like volumes are compared. If we do not refer to like volume, but to like number of molecules, we get the molar compressibility. If

$$\beta_M = -\frac{1}{v_M}\left(\frac{dv}{dp}\right)_M$$

is the compressibility of the medium, and

$$\beta_L = -\frac{1}{v_L}\left(\frac{dv}{dp}\right)_L$$

the compressibility of the solution, then we have an equal number of molecules when

$$v_M = \frac{M_M(n_M + n_L)}{\varrho_M}$$

and

$$v_L = \frac{M_M n_M + M_L n_L}{\varrho_L}$$

where M_M and M_L are the molecular weights of the medium and the dissolved substance, n_M, n_L and ϱ_M, ϱ_L the corresponding number of mols and the densities. If we put

$$\left(\frac{dv}{dp}\right)_M = 1$$

then

$$\beta' = \frac{\beta_L}{\beta_M}\frac{M_M n_M + M_L n_L}{M_M(n_M + n_L)}\cdot\frac{\varrho_M}{\varrho_L}$$

will be the change in volume occurring for equal change of pressure, referred to equal number of mols. and to the solvent as unit; this is therefore the relative molar compressibility.

Particularly in the case of sulphuric acid—water solutions, the β', c curve was much more plainly antibatic to the σ, c curve than was the β, c curve (see Fig. 15, A, B, and C). That the solubility curves of various gases, such as H_2, N_2, and O_2, in aqueous sulphuric acid, are also antibatic to the surface-tension curve, results from measurements of Christoff.

In other cases, a recalculation of this sort does not suffice to disclose a relationship between the σ, c and β, c curves; such is the case with some mixtures of liquids investigated by Skirrow and Ritzel. This is not surprising, since the surface tension depends upon the composition of the

[1] *loc. cit.* p. 44. [2] *loc. cit.* p. 44. [3] *loc. cit.* p. 44.

[4] Besides the references [1] to [3] also *Th. W. Richards* and *Palitzsch*, J. Amer. Chem. Soc. **41**, 59 (1919).

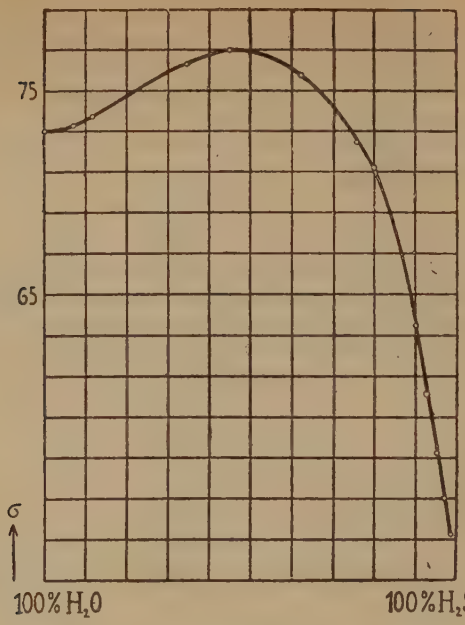


Fig. 15A.—σ, c Curve of aqueous H_2SO_4 Solutions.

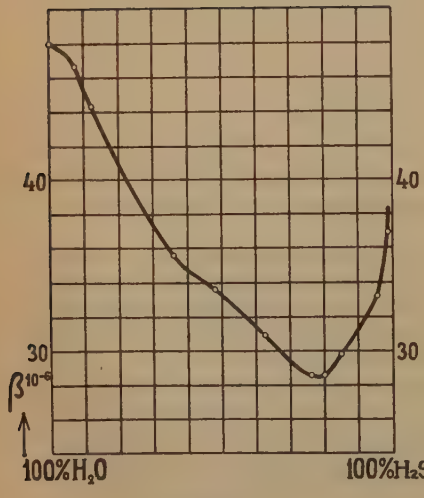


Fig. 15B.

β, c Curve of aqueous H_2SO_4 Solutions.

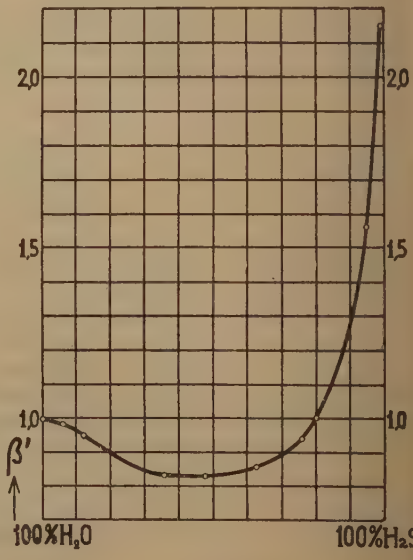


Fig. 15C.

β', c Curve of aqueous H_2SO_4 Solutions.

surface-layer, the compressibility upon the composition of the bulk of the liquid. One source of error must, however, still be considered, that in the case of the aqueous solutions of organic substances, small amounts of surface-active substances can simulate a decrease in σ. Thus, according to Ebeling,[1] the σ of sugar solutions increases with increasing concentration, and in accordance with theory the compressibility sinks; while, according to earlier experiments, the surface tension of sugar solutions diminished with increasing concentration, in contradiction to the theory; this anomaly was probably due to small quantities of an impurity.

The relation between capillary activity and tendency to dissolve has already been mentioned on p. 70.

The Adsorption of Gases at Liquid Surfaces

Hitherto we have supposed the gas space to be constant, and the concentration in the solution to change. The second case to be considered is the one in which the liquid remains practically unchanged, while the composition of the gas space is variable. This case is not often realized. Mercury in various gases probably approaches it fairly closely.

It differs distinctly in one point from the first case. If we have say a dilute aqueous solution, there can be no doubt that it is the surface tension water—water vapour which is influenced by the dissolved substance. But if we have, instead of mercury—mercury vapour, mercury in air (at atmospheric pressure), for example, we cannot well speak any longer of a change in the tension mercury—mercury vapour, but we have as second phase the air, in which some mercury vapour is dissolved, and hence a new tension mercury—air.

It is immediately evident that the argument on p. 47 which led to the Gibbs adsorption formula remains valid here as well, if we put in place of the osmotic pressure the partial pressure of the gas, the change of which is linked with the change of the surface tension. If now we consider the difficultly liquefiable gases, they are subject to the gas laws, whether they only form a small part, or the chief part, of the gas phase. We thus get the formula

$$\mathfrak{a} = -\frac{p}{RT}\frac{d\sigma}{dp}$$

where p is the partial pressure.

The law is therefore true: *A gas is negatively or positively adsorbed at a liquid surface, according as the surface tension increases or decreases with increase of partial pressure of the gas.* For this case, as already mentioned, Gibbs first enunciated his adsorption formula.

The formula has not yet been quantitatively proved, but much is known which shows a dependence of the surface tension upon the partial pressure of a gas, and hence an adsorption.

Firstly, the surface tension of a pure, non-associated liquid should give *in vacuo* a value of the surface tension completely independent of time, whereas in the presence of a gas the transition from a dynamic to a static surface tension should be observable. This is the case. Stöckle[2] determined the surface tension of pure mercury in a vacuum of about 0·0004–0·0010 mm. by the method of curvature measurement. The mirror-images, the size of which on the drops was measured, remained from the first (after

[1] *loc. cit.* p. 14. [2] *loc. cit.* p. 17.

about 5 sec.) completely unchanged; from sixty-seven observations on different drops, a mean value of $\sigma = 436$ dyne/cm. was obtained at 15°. Between the two extreme values there was a difference of 6 dyne/cm.

But if the drops were observed in a gas atmosphere, then even in the case of this pure mercury, and with the greatest precaution to keep away easily volatile and oily substances, which might lower the tension, an initial ageing of the surface occurred. In the case of all gases observed by Stöckle (H_2, O_2, N_2, CO_2, dry and moist air) the initial tension mercury—gas was greater than the tension mercury—mercury vapour; this large value sank in the course of 30 to 50 minutes to a constant value, which was the same or smaller than that found *in vacuo*. The following table shows this behaviour plainly.

TABLE 29

The Surface Tension of Mercury in various Gases

Gas.	σ (immediately after Production of Surface).	σ (after about 60 min.), Final Value.
Vacuum (15°)	436	436
Hydrogen (21°)	470	434
Oxygen (25°)	478	432
Nitrogen (16°)	489	438
Carbon dioxide (19°)	480	436
Dry air (17°)	476	429
Moist air (17°)	481	419

That this time-effect does not appear *in vacuo* proves that the mercury is not to be considered as an associated liquid, and that we are not dealing, as in the case of water, with an adsorption in the liquid. This is confirmed by the fact that the speed of condensation depends in a characteristic manner upon the nature of the gas. It is greatest in the case of hydrogen, smaller in the case of oxygen and carbon dioxide, still smaller in the case of nitrogen. A consequence of this is that in the case of a gas, such as hydrogen, with high adsorption velocity, considerably higher values of σ can be found by very quick measurement than are given as initial values in Table 29. G. Meyer [1] actually found by the method of vibrating jets, which allows of the measurement of a surface not yet one second old, values of σ for mercury in hydrogen = 554, in oxygen = 504, while the value for carbon dioxide = 487, and for nitrogen = 496, were only slightly different from those given in Table 29.

The same is true for the velocity of adsorption, as was said on p. 50. It is therefore great, and the process which requires a finite time is a diffusion in a very thin layer. The equilibrium is therefore mostly reached in a few minutes. In agreement with the high diffusion constant of hydrogen is the especially rapid attainment of equilibrium in the case of this gas.

Since the gases are positively adsorbed at a mercury surface, it is to be expected that the σ of mercury should fall with increase in gas pressure. This is so according to Kundt [2] for the interface mercury—air.

The general case, that the gas is fairly soluble in the liquid, brings

[1] Wied. Ann. **66**, 523 (1898). [2] Wied. Ann. **12**, 538 (1881).

nothing new. If the gas pressure increases, the concentration of the gas in the solution must also increase; if therefore σ changes in the same direction as the gas pressure, it must change in the same direction as the concentration in the solution. The Gibbs adsorption equation

$$a = -\frac{p}{RT}\frac{d\sigma}{dp}$$

remains therefore unchanged; since Henry's law must be valid—the formula is only deduced upon this assumption (see p. 48)—it is a matter of indifference whether the change in σ is referred to the partial pressure or to the concentration in solution.

Since the condensed gases have very low surface tensions (see Table 2 and p. 53) we may expect that the σ of gas solutions will decrease with increase of pressure. Kundt [1] investigated the surface tension by the method of capillary rise for the liquids alcohol, alcoholic solution of $CaCl_2$, ether, chloroform, carbon disulphide, water, and the gases hydrogen, carbon dioxide, and air, for increasing gas pressures (up to 150–200 kg./sq. cm.), and actually found that σ decreases in all cases with increase of gas pressure; and further, in entire agreement with considerations to be discussed later (cf. p. 120), $\frac{d\sigma}{dp}$ for air and carbon dioxide is greater than for hydrogen. The σ, p curves are slightly convex to the axis of p, which is indeed mostly so in other cases where a lowering of σ takes place (cf. p. 54).

In agreement with this are experiments on the surface tension of gas solutions, which were carried out by Bönicke.[2] According to Kundt, the σ of water against air sinks for a rise of pressure of 1 atmosphere by about 1 per cent. The tension of air-free water against a vacuum is also, according to Bönicke, greater by just this amount as compared with the tension of water saturated with air against air. This was confirmed by Magini.[3] Solutions also of carbon dioxide, nitrous oxide, and hydrogen sulphide in water showed lowerings of the tension of pure water of 1–3 per cent. (temperature 18°).

A statement of Lenard [4] is in apparent contradiction to this, that if air is allowed to come into contact with a water surface, which has taken up a constant value of the surface tension *in vacuo*, no noticeable change in σ (less than 0·5 per cent.) takes place; only after some time did he observe a lowering, which he wished to ascribe to the influence of other foreign substances. It is not perhaps impossible that the saturation of the liquid surface may also proceed comparatively slowly. The reader may be reminded (cf. p. 52) that water also shows an ageing effect *in vacuo*, which is to be ascribed to the adsorption of one of the kinds of molecules present in water.

In the case of liquids with small surface tension, such as the organic liquids, the change in σ produced by the dissolving of gas is mostly small.[5] Ferguson [6] compared the surface tension of several liquids (water, ethyl

[1] *loc. cit.* p. 82.

[2] "Über den Einfluss absorbierter Gase auf die Oberflächenspannung des Wassers." Diss., Münster, 1905.

[3] Atti R. Accad. d. Lincei, **20,** I. 30 (1911).

[4] Sitzungsber. d. Heidelb. Akad. 1910, 18 Abh. p. 6 et seq.

[5] Among others *Whatmough, loc. cit.* p. 22; *Christoff,* Zeitschr. f. physik. Chem. **79,** 456 (1912).

[6] Phil. Mag. (6), **28,** 403 (1914).

alcohol, ethyl ether, chloroform, benzene, and others) against air and against CO_2 and found the value in CO_2 to be about 1–2 per cent. smaller.

In any case it appears from these experimental results that it makes very little difference whether the surface tension of liquids with small and medium σ values is measured *in vacuo* or in contact with air (cf. p. 25).

The Rate of Rise in Capillaries

Décharme [1] investigated this process very thoroughly for pure liquids and for solutions. It is, as we should expect, fairly complicated, since the driving force changes with the distance between the momentary height and the maximum height. As a first approximation the course is logarithmic, but there is another influence unmistakably at work, which depresses the speed of rise as equilibrium is approached to a greater degree than the logarithmic formula requires. We require an equation with three constants to represent the observed values within the limits of error.

If we are at a great distance from the final equilibrium, the driving force may be regarded as constant, and the motion of the liquid in the capillary may be expected to follow Poiseuille's law. This is actually the case (cf. p. 694) as soon as we pass to fine capillaries, such as are present in filter paper, earthenware plates, and the like. In these the motion of the liquid is so slow, and the height of rise is so great, that the motion of the liquid may readily be followed in a region in which the driving force is practically constant. In the case of quick rise in comparatively coarse capillaries such as were used by Décharme, a supposition of this sort is not permissible.

But the Poiseuille law may be applied, as Bell and Cameron [2] showed, if we reverse matters and measure the velocity with which a liquid approaches the equilibrium position when it has been drawn up far above the height of rise. They arranged the experiments in such a way that they sucked the liquid into a capillary tube which dipped into the liquid, and was bent round horizontally above the height of rise, and they then followed the return of the thread of liquid against a scale after the suction had been stopped. According to Poiseuille's law, the volume of liquid v flowing in unit time out of a capillary of radius r is given by the equation

$$v = \frac{\pi\eta}{8}\cdot\frac{r^4 H\varrho}{l} \qquad \ldots\ldots\ldots (1)$$

Here H is the head of liquid under which the flow takes place, ϱ the density of the liquid, and l the length of the capillary. If we measure the velocity of outflow by means of the change of length of the liquid column in the capillary, as in Bell and Cameron's experiments, v may be replaced by the differential quotient $\frac{dl}{dt}$. If we are sufficiently removed from equilibrium then H may be taken as constant, and r also. If all constant quantities are united to a single one k, then we have

$$\frac{dl}{dt} = \frac{k}{l} \qquad \ldots\ldots\ldots (2)$$

which integrated gives

$$(l_2^2 - l_1^2) = k(t_2 - t_1). \qquad \ldots\ldots\ldots (3)$$

[1] Ann. de chim. et de phys. (4), **27**, 228 (1872); **29**, 415, 564 (1872); (5) **1**, 145, 318 (1873).

[2] J. physic. Chem. **10**, 658 (1906).

For the case we are dealing with, if y is the length of the vertical tube, and x the length of the thread of liquid in the horizontal part, then

$$(x_2 + y)^2 - (x_1 + y)^2 = k(t_2 - t_1).$$

This equation could be well confirmed. The exponent had actually the value 2.

Since the viscosity decreases with increase of the temperature, the velocity of rise increases with the temperature, while the state of equilibrium which is approached, the height of rise that is to say, decreases with rise of temperature. This is therefore a case in which the speed of the process is increased by rise of temperature, while the equilibrium is displaced in the opposite direction.

II. The Interface Liquid—Liquid

General. Methods of Measurement

For the boundary surface or interface between two liquids which are not miscible in all proportions the same is true as for the boundary surface liquid—gas. Since both phases are easily mobile, the interface can take the form which the tension ruling in it requires. A liquid disseminated in small quantities in another appears in the spherical form ; the phenomenon of rise in capillaries may be observed, surface waves may be generated, and so on.

All the methods described on pp. 12 to 23 may be in principle applied to the measurement of the interfacial tension liquid—liquid. Also, as regards the theory of the phenomenon, there is little new to be said. In the first place, everything that was stated on p. 46 is valid. We have only to remember that here we are in the end always dealing with solutions. For the one liquid will always be soluble in the other to some degree, however small. Hence the *dynamic* tension of liquids, when first brought into contact, is to be distinguished from the *static* tension, when the two liquids are mutually saturated. Not only do liquids which are not miscible in all proportions have a mutual surface tension · even two completely miscible liquids, before they have united to form one phase, exhibit a dynamic interfacial tension. For we get by careful overlaying of any two liquids a definite meniscus, a jet of one liquid may be generated in another, and so on. This tension decreases rapidly during the process of solution, and becomes zero as soon as the two liquids have mixed completely.

As regards the practical measurement of the interfacial tension between liquids, all well-defined methods previously mentioned have been used :

Vibrating jets.[1]

Vibrating drops.[2]

Surface waves.[3]

[1] *G. Meyer*, Verh. d. deutsch. physik. Ges., **17**, 46 (1898) ; Physik. Zeitschr. **12**, 975, (1911).

[2] *K. Boedeker*, Ann. d. Physik. (4), **46**, 503 (1915). They were not, as in *Lenard's* case (see p. 14), generated by the action of gravity, but by alternating electric fields ; these acted upon drops of water, which swam in non-conducting liquids of as far as possible equal density (e.g. a mixture of CCl_4 and oil of turpentine).

[3] *Watson*, Phys. Rev. **12**, 257 (1901).

Drop-curvature [1] and dimensions of large flat drops.[2]
Capillary rise.[3]
Adhesion rings and plates.[4]
Drop-weight [5] and drop-pressure,[6] etc.

The same formulæ hold that were given previously. We have only to remember that in the case of the surface tension liquid—gas the density of the gas can generally be neglected as compared with that of the liquid, while in the case of two liquids this may not be done ; that is, the buoyancy must always be taken into account. Thus, for the measurement of the capillary rise, we obtain the formula

$$\sigma = \tfrac{1}{2} rhg(\varrho_1 - \varrho_2)$$

where ϱ_1 and ϱ_2 are the densities of the two liquids ; for the interfacial tension has no longer to hold up the whole weight of the raised liquid column ; this weight is to be reduced by the weight which the other liquid would have if it filled the same space.

As regards the measurement it should further be remarked that in the case of the method of capillary rise the proper wetting of the tube-wall must be attended to. As the comparison with the phenomena of liquid—gas surfaces tells us, that liquid which has a concave meniscus against the other must wet the tube.

The great similarity between the phenomena at the interface liquid—liquid and liquid—gas was early recognized. Quincke [7] was the first to measure a large number of such tensions between different liquids, and to trace their relation to the tensions of the pure liquids against air.

Of late the tension at the surface of mercury in contact with aqueous solutions has been measured particularly often, with the object of explaining capillary-electrical phenomena.

Static and Dynamic Tension between Liquid and Liquid

The following table contains a number of static interfacial tensions, measured by different observers and by different methods. We see at once from the numbers that the σ values are of the same order of magnitude as those for the tension liquid—gas, although they are in general somewhat smaller.

The dynamic interfacial tensions between two completely miscible liquids are naturally much smaller. Quincke [8] measured by the method of drop-weight the dynamic tension of ethyl alcohol in contact with aqueous salt solutions (sulphate of zinc, copper, etc.). In these the drop, as it emerges, does not pass into streaks, but keeps at first its shape. He found values

[1] *König*, Wied. Ann. **16**, 1 (1882).
[2] *Quincke*, Pogg. Ann. **139**, 27 (1870) ; *Lenkewitz*, "Untersuchungen über Kapillarität." Münster, 1904.
[3] *v. Lerch*, Ann. d. Physik (4), **9**, 434 (1902) ; *van der Noot*, Bull. de l'Acad. R. d. Belg. 1911, p. 493.
[4] *A. Pockels*, Wied. Ann. **67**, 668 (1899) ; further also *Watson* (cf. under [3] on p. 85).
[5] *Antonow*, J. d. Chim. Phys. **5**, 372 (1907) ; *W. C. McC. Lewis*, Phil. Mag. (6), **15**, 499 (1908) ; *Harkins* and *Humphery*, J. Amer. Chem. Soc. **38**, 236 (1916) ; *Harkins* and *Grafton*, J. Amer. Chem. Soc. **42**, 2534 (1920) ; *Harkins* and *Ewing*, J. Amer. Chem. Soc. **42**, 2539 (1920).
[6] *Cantor*, Wied. Ann. **47**, 399 (1892).
[7] *loc. cit.* under [2].
[8] Ann. d. Physik. (4), **9**, 11 (1902).

TABLE 30

Interfacial Tensions of various Pairs of Liquids

Pair of Liquids.	Method.	σ_g.	Observer.
Mercury—water (20°)	Drop-weight	374·8	Harkins and Grafton [1]
Mercury—alcohol (20°)	,,	364·3	,, ,, [2]
Mercury—benzene (20°)	,,	362·8	,, ,,
Water—petroleum hydrocarbon (16°)	,,	48	W. C. McC. Lewis [3]
Water—benzene (20°)	,,	32·6	Antonow [4]
Water—isobutyl alcohol (20°) . .	,,	1·76	,,
Water—isoamyl alcohol (20°) . .	,,	4·42	,,
Water—ethyl ether (20°) . . .	,,	9·69	,,
Water—chloroform (20°) . . .	,,	27·7	,,
Water—carbon tetrachloride (22°) .	Cap. rise	43·4	Lóránt [5]
Methyl alcohol—carbon disulphide (18°)	Drop-weight	0·82	Antonow [4]

between 0·8 and 3 dyne/cm. The method of vibrating jets should be particularly applicable to the measurement of these tensions.

The Interfacial Tension Liquid—Liquid of Solutions

When we now speak of solutions, we are not referring simply to the fact that in the case of the tension liquid—liquid we are always dealing with solutions, since the two liquids are always soluble to some extent in one another, but to solutions of third substances, which are present preferentially in either liquid or both. In almost all cases water is one of the liquids concerned, and we have then the same state of affairs as was discussed on p. 55, viz. *surface-inactive* solutions, particularly those of the inorganic salts, in which the surface tension changes very little with the concentration, and *surface-active* solutions in the case of the fatty acids, alcohols, and other organic substances, in which the interfacial tension decreases greatly with increase of concentration. This is evident from measurements by v. Lerch,[6] σ_g of water—benzene in presence of inorganic and organic acids, bases, and salts according to the capillary-rise method; by Bubanovič,[7] σ_g of water—olive oil in presence of organic substances with the stalagmometer; by Lóránt,[8] σ_g of water—ethyl ether, —chloroform, —nitro-benzene, —carbon tetrachloride, particularly in presence of inorganic salts, according to the capillary-rise method and with the stalagmometer.

In the case of the *capillary-inactive* solutions the changes are in general so small that the σ_g, c curves can be regarded as straight lines. The lyotropic series is, according to Lóránt, pronounced for inorganic salts; however, it depends upon the pair of phases whether σ_g is lowered or raised; in the case of the very small tension water—ethyl ether most electrolytes raised the tension, only iodides and thiocyanates lowered it; while in the case of

[1] *loc. cit.* p. 86.
[2] *Lenkewitz* (*loc. cit.* p. 86) in good agreement with method of flat drops.
[3] *loc. cit.* p. 86.
[4] *loc. cit.* p. 86.
[5] Pflüger's Archiv, **157**, 211 (1914).
[6] *loc. cit.* p. 86.
[7] Meddel. fr. K. Vetensk. Nobelinstitut. **2**, Nr. 17 (1911).
[8] *loc. cit.* under [5].

pairs of liquids with higher tension, more and more salts were found to lower the tension; in the case of the tension water—carbon tetrachloride, for example, besides iodides and thiocyanates, also bromides, sulphates, $CaCl_2$, $FeCl_3$ lowered the tension, and only NaCl and KCl raised it.

In the case of the *capillary-active* solutions the σ_g, c curves are, as in the case of the surface tension, strongly convex to the c axis; here also, with increase of concentration, a value of σ_g is reached which scarcely changes further. The strongly bent part of the curve for more dilute solutions could be very well expressed by the formula of v. Szyszkowski (see p. 62)

$$\frac{\sigma_M - \sigma_L}{\sigma_M} = \Delta = \mathrm{b} \log \left(\frac{c}{\mathrm{c}} + 1 \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

As example we may give from Bubanovič the tension water—olive oil as lowered by *n*-butyric acid.

TABLE 31

Lowering of σ_g Water—Olive Oil by *n*-Butyric Acid. $t = 23°$

$b = 0{\cdot}1455$; $c = 0{\cdot}02613$

c (Mol. per L.)	σ_g (obs.).	σ_g (calc.).
1	20·0	—
∞		
0·025	18·1	18·2
0·050	17·0	16·9
0·10	15·4	15·4
0·20	13·7	13·7
0·50	11·2	11·3
1·00	9·2	9·3

Here also b has the same value of about 0·2 for the different solutes, while c varies greatly.

The general parabolic equation (cf. p. 66)

$$\frac{\sigma_M - \sigma_L}{\sigma_M} = \Delta = sc^{\frac{1}{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

again usually suffices; the same limitation as before must, however, be made. The $\log_{10}\Delta$, $\log_{10}c$ curve is not strictly straight, as it should be according to equation (2), but is distinctly concave to the $\log_{10}c$ axis. The value of $\frac{1}{n}$ lies here again in the neighbourhood of 0·5. More extended series of experiments upon surface-active organic substances of the homologous series are not available. That Traube's rule is also true here appears from some experiments of Harkins and Humphery [1] on the alteration in the interfacial tension water—benzene by fatty acids.

The comparison with surface tension must not however be carried too far, and it should always be remembered that the circumstances can become very different on account of the fact that in the case of surface tension we have the gas space as second phase, in the case of interfacial tension a liquid with quite different conditions of solubility. If the vapour space is the second phase, as in the case of surface tension, then taking for example the

[1] J. Amer. Chem. Soc. **38**, 242 (1916).

aqueous solutions of the fatty acids, the distribution will always be in favour of the water-phase, and it is logical and permissible if we refer, in making comparisons, to the concentration in the aqueous phase. But this is by no means self-evident, if we have an oil as second phase along with water. Here the solubility of a fatty acid may possibly be greater in oil than in water, and the direction of the distribution may actually reverse as we go up the homologous series. It is further very probable that capillary activity is exhibited only in liquids which, like water, have a high internal pressure, hence a large surface tension against the gas space, and not in liquids with a low internal pressure and small surface tension, such as the organic liquids. If now the active dissolved substance, say the fatty acid, is chiefly dissolved in water, then the interfacial tension can be decidedly lowered; if it is chiefly contained in the oil, the interfacial tension will probably only be slightly influenced. Only with a second phase, which takes up as little or less of the substances dissolved in water than does the vapour space (for example, mercury) can we expect that the state of affairs will be like that in the case of surface tension.

These relationships have not yet been submitted to a detailed and consistent investigation. Nevertheless some results may already be interpreted from this point of view. Thus Bubanovič found capillary activity on the part of *n*-butyric acid and chloral hydrate at the interface water—olive oil, while many other organic substances, such as ethyl alcohol, chloroform, benzene, xylene, oil of turpentine, which are decidedly active for the surface water—air, had practically no influence upon water—olive oil.

Then, further, is the fact that at the interface water—oil the salts of the higher fatty acids, the soaps, are sensibly more active than the fatty acids themselves, which is not true of the surface tension. Reinders [1] measured the drop-weight of an oil which contained increasing quantities of a fatty acid (oleic and stearic acids respectively), against aqueous solutions, the $H^{\cdot}$ and OH' ion content of which was buffered in a known manner by mixtures of phosphoric acid with the sodium phosphates. The drop-weight and hence the interfacial tension certainly declined with increase in fatty acid content. But the great decline in the interfacial tension with neutralization of the first and particularly the second hydrogen atom of the phosphoric acid, was much more remarkable; that is, in precisely that range of concentration in which the OH' ion concentration increases particularly rapidly, and the $H^{\cdot}$ ion concentration therefore decreases. The drop-weight could actually be represented as a linear function of the logarithm of the $H^{\cdot}$ ion concentration, a relation which reminds us of Milner's (p. 63). Reinders ascribes this effect of the OH' ions to the formation of a strongly surface-active soap, in agreement with which is the fact that the depression of σ_{fl} at the second neutral point (saturation of Na_2HPO_4) is greater, the greater the content in fatty acid, the greater the quantity of soap formed. That the soap is more strongly active than the acid is explained from what has been said above, by the fact that, although it is difficultly soluble in both liquids, it will be chiefly active in the water, while the fatty acid, which is readily soluble in the oil, will have a less effect precisely on account of this solubility.

Further detail with regard to the capillary activity of soap solutions, which belong to the colloidal solutions, follows at a later place (p. 536).

[1] *Van Bemmelen*-Festschrift, p. 333 (1910).

Dubrisay [1] has worked out a method for the titration of acids based upon the strong lowering of the interfacial tension by small amounts of soap, after v. Lerch [2] had already drawn attention to such a possibility. He determined with aid of the drop-weight or drop-number the σ_{fl} of a vaseline oil containing stearic or oleic acid against the aqueous acid solution to be investigated, which was gradually neutralized by addition of alkali. The first small excess of alkali betrayed itself in a great lowering of the drop-weight or raising of the drop-number, caused by the formation of a small amount of soap.

We may here refer to the experiment of Brailsford Robertson,[3] which is important for the understanding of the nature of cell-division. If a thread moistened with alkali or soap solution be laid over a small drop of oil floating on water and containing some fatty acid, then the drop divides into two parts through the plane marked by the thread. The division commences by the drop getting a deep depression at the points where the thread passes through the interface oil—water, and the drop is then torn in halves by the currents which go out from this middle position to the ends of the drop. Here again we are dealing with a lowering of the interfacial tension caused by the soap, which produces the motion described above (p. 70) from places of lower to places of higher interfacial tension. It is quite possible that cell-division depends upon similar processes, only that internal processes going on in the cell itself bring about in that case the lowering of the interfacial tension in an equatorial plane.

In connexion with the circumstance just discussed, that the state of affairs in the case of surface tension cannot be assumed in the case of interfacial tension without further question, we have further the fact that the inorganic electrolytes which are throughout inactive as regards the surface tension sometimes lower the interfacial tension decidedly. For example, W. C. McC. Lewis [4] found for the interface water—petroleum hydrocarbon that even KCl has a decided action in this sense, and $BaCl_2$, $CaCl_2$, etc., a still stronger one. The σ, c curve resembled throughout that observed in the case of capillary-active substances. There is no reason which compels us to assume that, if the surface tension of the molten electrolyte against the gas space were greater than that of water at the same temperature, the interfacial tension of the molten salts against the second liquid would have to be as much or even at all greater than the interfacial tension of the water against the second liquid; it might be of the same amount, or even smaller. If we again start from the consideration of the general σ, c curve (cf. p. 55) we should only expect in the first case (that of surface tension) that σ would increase with increasing concentration of electrolyte; in the second case (that of interfacial tension) it might very well decrease. It therefore appears entirely unconvincing when W. C. McC. Lewis [5] finds a contradiction in the fact that the electrolytes are not always inactive at interfaces, and when he attempts to remove it by introducing in place of the surface or interfacial tensions another quantity, which decreases also in the case of surface tension with increase of electrolyte concentration.

[1] Bull. Soc. Chim. France (4), **13**, 657 (1913).
[2] *loc. cit.* p. 86.
[3] Arch. f. Entwicklungsmechanik, **27**, 29 (1909).
[4] Phil. Mag. (6), **17**, 466 (1909).
[5] Zeitschr. f. physik. Chemie, **74**, 619 (1910).

Adsorption at the Interface Liquid—Liquid

Since the interfacial tension is defined exactly as is the surface tension liquid—gas, the same considerations may be advanced as on p. 46. The Gibbs adsorption formula is therefore valid (cf. p. 48)—

$$\mathfrak{a} = -f(c, \mathrm{T} \ldots) \frac{d\sigma_g}{dc}$$

or, if van 't Hoff's laws hold in the solution,

$$\mathfrak{a} = -\frac{c}{\mathrm{RT}} \frac{d\sigma_g}{dc},$$

that is, a dissolved substance will be positively adsorbed, if it lowers the interfacial tension, negatively if it raises it.

The measurement of this adsorption is perhaps not quite so difficult as for the interface liquid—gas, for in a liquid finely divided drops do not unite quite so quickly as a foam disappears. Experiments of this sort were undertaken at Donnan's suggestion by W. C. McC. Lewis,[1] further by Patrick.[2] Lewis measured the adsorption at the interface water—petroleum hydrocarbon for electrolytes such as KCl, $BaCl_2$, $CuCl_2$, etc.; then also for caffeine and for substances of high molecular weight such as sodium glycocholate, etc.; further for aniline at the interface water—mercury. Patrick determined for the interface water—mercury the adsorption of mercurous nitrate, salicylic acid, picric acid, neufuchsin, etc. In the case of the hydrocarbon the experiments were carried out by two methods. According to the first it was emulsified in the aqueous solution, and the size of the drops was then determined under the microscope, from which the area of the adsorbing surface could be deduced. The amount of change in the content of the solution after the distribution of the drops in it was determined by measuring the tension of the hydrocarbon on the one hand against the original solution, and on the other against the emulsion. A rise in the tension was actually observed, that is, a diminution in the concentration caused by adsorption on the drops. According to the second method, the drops of hydrocarbon rose, as in the experiments of Donnan and Barker (cf. p. 74), through a long column of the aqueous solution and collected in a suitably divided vessel, so that a subsequent backward diffusion of the solute given up by the drops after coalescence was avoided as far as possible. The change in the content of the liquid column was determined by drop-number, or gravimetrically. In the case of mercury, both Lewis and Patrick allowed a stream of fine drops of mercury to fall through a long column of the aqueous solution, and determined subsequently the concentration in the liquid; Lewis again used for this purpose the change in the tension, while Patrick determined directly the concentration, either gravimetrically or colorimetrically. A cause of disturbance in these measurements is the fact that the mercury drops, upon coalescing at the bottom, again give up the adsorbed material, and that this then rapidly redistributes itself in the whole liquid column on account of the lively stirring which the stream of drops causes; in this way the change of concentration caused by the adsorption is nullified to a great extent. Patrick remedied this disturbance by causing the aqueous solution to flow slowly in a contrary direction to

[1] Phil. Mag. (6), **15**, 499 (1908); **17**, 466 (1909); Zeitschr. f. physik. Chemie, **73**, 129 (1910).

[2] Zeitschr. f. physik. Chemie, **86**, 545 (1914).

the stream of mercury, and allowed it to flow out near the point of entry of the latter.

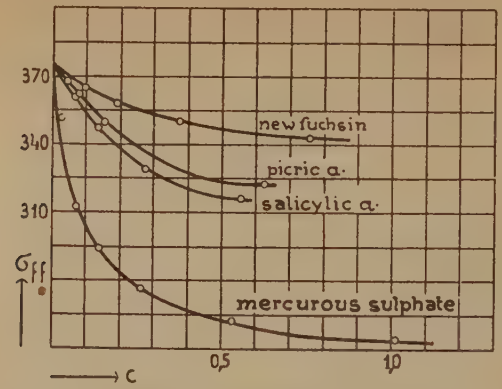


Fig. 16A.—σ_{ff}, c Curves for the Interface Mercury—Aqueous Solution.

The experiments showed that an adsorption is undoubtedly present, which is connected with the lowering of the σ_{ff} by the dissolved material.

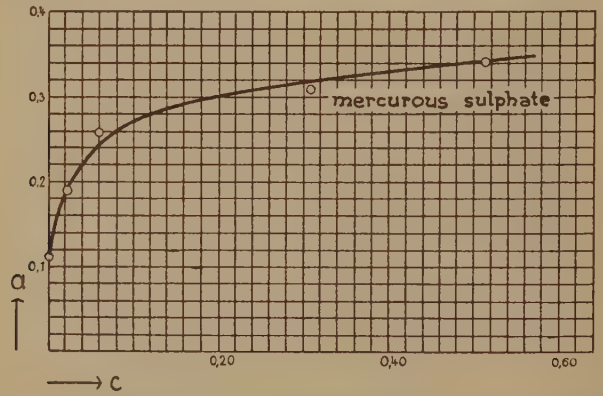


Fig. 16B.—Adsorption at the Interface Mercury—Aqueous Solution.

This is mostly plainly seen in two figures from Patrick's paper, of which the one (Fig. 16A) gives the dependence of the σ_{ff} water—mercury upon the

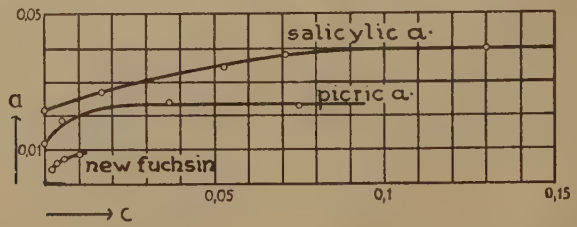


Fig. 16C.—Adsorption at the Interface Mercury—Aqueous Solution.

concentration of the dissolved substances, while Figs. 16B and C represent the quantity adsorbed as a function of the concentration (the c values are

given in millimol per litre, the a values in a relative measure). We see that the order of adsorption of the four substances mercurous nitrate, salicylic acid, picric acid, neufuchsin, is the same as that in which they depress σ_g. Morphine hydrochloride and caffeine depress σ_g still less; and accordingly the adsorption is so small that it cannot be determined by the existing analytical methods.

Objections might be raised to these experiments in that, in the case of mercury, electro-capillary influences which will be discussed later (p. 287) must be largely taken into account. These objections are met by the fact that the experiments were carried out under completely comparable conditions, and that it is not a question of the one-sided taking up of one ion, but that in two cases—mercurous nitrate and neufuchsin—the content of cation was determined, and in two others—salicylic and picric acids—the content of anion. It was also expressly proved that the concentration of the substances named does not change when they simply stand over mercury.

As regards the validity of the simple Gibbs adsorption formula (formula 3, p. 48) it cannot be tested by means of Patrick's experiments, since the counter-current method used by him only gives relative values. The measurements of Lewis are perhaps less exact, but approach nearer to being absolute. In the case of the adsorption of the electrolytes KCl, $CuCl_2$, and $AgNO_3$ at the interface water—petroleum, the formula was not confirmed; the observed values of the adsorbed amount a lay in the order of magnitude of about 10^{-8} gm./sq. cm., the values calculated from the lowering of the interfacial tension were of the order 10^{-9}. In the case of the non-electrolytes investigated by Lewis (caffeine at the interface water—petroleum, aniline at the interface water—mercury) the adsorbed amount was below or at the limit of analytical detection, which did not contradict the values calculated from σ_g. In the case of electrolytes circumstances may very well be such that the assumptions upon which the validity of the Gibbs law depends are not fulfilled.

Attention may also be drawn to the form of the adsorption curve as it appears from Figs. 16B and C; a surprisingly large amount adsorbed at low concentrations; a growth, as the concentration rises, which is not in proportion, but rises much less slowly; and finally at high concentrations a saturation, which hardly changes. This course entirely corresponds to the adsorption at solid boundaries. For this, as we shall see later on, p. 172, the equation

$$a = \alpha c^{\frac{1}{n}}$$

holds. Here a is the amount adsorbed; α and $\frac{1}{n}$ are constants. The formula is only valid at some distance from saturation, and can only be applied to the bent rise of the curve, upon which, in Patrick's experiments, not too many points fall.[1] Hence in the following table only one numerical example is given, in order to afford an approximate idea of the change of concentration.

The amount adsorbed is here simply the difference between the original concentration and the final concentration, which was reached with a steady stream of mercury and counter-current of solution.

[1] The curve for neufuchsin, which falls entirely in this range, also agrees satisfactorily with this equation.

Table 32

Adsorption of Salicylic Acid at the Interface Water—Mercury
Room Temp.

Original Conc. Millimol/Litre.	Final Conc. c Millimol/Litre.	Adsorbed Amount. Millimol/Litre.
0·022	0·000	0·022
0·044	0·017	0·027
0·087	0·053	0·034
0·109	0·071	0·038
0·218	0·178	0·040

Lewis tried in vain to measure in the case of the adsorption of sodium glycocholate at the interface water—petroleum a *heat of adsorption*. But he was able to show, from the change in the sign of the temperature coefficient of the interfacial tension, that the heat of adsorption must be positive. That the temperature coefficient γ for the pure system water—petroleum is positive appears from Table 33, p. 95. In the case of the solution of the salt of glycocholic acid (3 grams per litre), on the other hand, a negative value, $\gamma = -0{\cdot}004$, was obtained. The tension rises therefore in the case of the solution with rise of temperature (11·76 dyne/cm. at 16° to 14·4 dyne/cm. at 67°) and falls in the case of pure liquids (from 48 dyne/cm. at 16° to 37·1 at 67°). The lowering of σ_β at higher temperatures is obviously less, hence less is adsorbed at higher temperatures. Since therefore the adsorption is favoured by fall of temperature, the heat of adsorption must be positive according to the principle of van 't Hoff and le Chatelier.

As regards the *velocity of adsorption* the transition from dynamic to static tension is no longer a measure of it, as was previously the case (p. 50), for now it is not merely a question of the concentration of the dissolved substance at the interface, but also of the diffusion of the two liquids into one another. But it may be regarded as certain that equilibrium at the interface is reached in a short time—only a few seconds or minutes; for the stationary state, which was set up in Patrick's experiments, was reached in a few minutes.

Influence of Temperature upon the Interfacial Tension Liquid—Liquid

The interfacial tension between two liquids which are not miscible in all proportions becomes zero at the critical solution-point of the two liquids; this may be either a lower or an upper.

In the first case, the interfacial tension declines, in general, with rise of temperature, in the second it increases. The further fact must be taken into account that we are always dealing with solutions, and that we are comparing phases of different concentration at different temperatures. For the composition of the two phases, which are in equilibrium, changes with the temperature. The conditions are therefore never so simple as in the case of the surface tension of a pure, non-associated liquid.

Few measurements of the influence of temperature upon interfacial tension are available. If we assume for the present that here also the

tension changes, as a first approximation, linearly with the temperature, according, that is, to an equation

$$\sigma_{g\,t} = \sigma_{g\,0}[1 - \gamma(t - t_0)],$$

we find that the value of γ differs little in order of magnitude from the values found for the surface tension.

The following table contains a few values of γ; in the calculation the σ_g value for the lower temperature was taken simply for $\sigma_{g\,0}$. In the case of water—ether, therefore, the interfacial tension rises with the temperature. The same result was obtained by Morgan and Evans [1] for water—triethylamine. They also obtained a very complicated course for the temperature dependence of the tension water—phenol, which is most probably to be referred to the same causes as the peculiar dependence of the surface tension of aqueous phenol solutions (cf. p. 76).

TABLE 33

Influence of Temperature upon the Interfacial Tension σ_g

Pair of Liquids.	$\sigma_{g\,0}$.	γ.	Observer.
Mercury—benzene . . .	342 (20°)	+ 0·004	Cantor [2]
Water—petroleum . . .	48 (16°)	+ 0·005	W. C. McC. Lewis [3]
Water—ethyl ether . . .	9·12 (14°)	− 0·009	Antonow [4]

How the interfacial tension changes in the neighbourhood of the critical point of mixture will be dealt with later, p. 100, in connexion with the behaviour of the surface tension of the separate liquid phases.

Any sort of simple relation akin to Eötvös' rule is only to be expected under certain conditions, since we are always dealing with solutions (cf. p. 76).

In the case of solutions of third substances, very complicated relations will appear, as was already suggested above, p. 94, in discussing the heat of adsorption. In general, a similar connexion with the change of tendency to solution will exist, as we have become acquainted with in the case of the dependence of the surface tension of solutions upon temperature (see p. 76).

Influence of the Pressure upon the Interfacial Tension Liquid—Liquid

While at the interface liquid—gas the influence of a change of pressure cannot be followed, it may be determined for the interface between two liquids. Lynde [5] made experiments of this kind as follows: The height of rise of one of the liquids was determined in a capillary tube, which projected into another liquid. This latter filled the interior of the pressure bomb, and permitted the pressure to be transmitted. Two windows opposite to one another allowed the motions of the meniscus to be measured. The fact must be taken into account that the pressure both changes the height of rise directly and indirectly, since it changes the density. If

$$\sigma_g = \frac{1}{2} rgh(\varrho_1 - \varrho_2)$$

[1] J. Amer. Chem. Soc. **39**, 2151 (1917). [2] *loc. cit.* p. 86.
[3] *loc. cit.* p. 86. [4] *loc. cit.* p. 87. [5] Phys. Rev. **22**, 181 (1906).

is the equation for the height of rise, then

$$\frac{d\sigma}{dp} = \frac{1}{2}rg(\varrho_1 - \varrho_2)\frac{\delta h}{\delta p} + \frac{1}{2}rgh\left(\frac{\delta\varrho_1}{\delta p} - \frac{\delta\varrho_2}{\delta p}\right).$$

If we divide by the first equation, we get

$$\frac{1}{\sigma_g}\frac{d\sigma_g}{dp} = \frac{1}{h}\frac{\delta h}{\delta p} + \frac{1}{\varrho_1 - \varrho_2}\left(\frac{\delta\varrho_1}{\delta p} - \frac{\delta\varrho_2}{\delta p}\right).$$

The first quantity on the right is obtained from observation, the second is deduced from the compressibilities of the two liquids.

For the relative percentage coefficient of pressure

$$\left(\frac{100}{\sigma}\frac{d\sigma}{dp}\right)$$

both positive values (in the case of mercury—water, mercury—ether, water—carbon disulphide) and negative ones (in the case of water—ether, water—chloroform) were found. Its absolute value was about 1 per cent. for mercury—water and water—chloroform, 3 per cent. for water—CS_2, and 20 per cent. for water—ether for a change of pressure up to 3,000 kg. Within this range the pressure coefficient of the interfacial tension is a linear function of the pressure. Unquestionably, its sign and magnitude is closely connected with the dependence upon pressure of the mutual solubility of the two liquids, of which little is known.

The Interfacial Tension between two Liquids and their Surface Tensions against the Gas Space

The question of a symbasis between interfacial tension and surface tension was shortly discussed above, p. 88. Also, in the case of the phenomena of motion described upon p. 70 under the influence of the vapour of a capillary-active substance, we are dealing fundamentally with the interaction of surface tension and interfacial tension. This relationship will now be discussed. It is made obvious to the eye through the movements which occur on contact of two liquids of greatly different surface tension, and are so well known from the behaviour of water towards alcohol, that it is not necessary to describe them in detail. The essential fact is that a drop of a liquid B brought upon the surface of a liquid A does not in general remain still, but spreads out in a thin layer upon the surface of the liquid A.

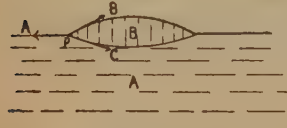


Fig. 17.

The question is, under what conditions does such a spreading-out take place? If the drop of B is situated upon A as represented in Fig. 17, the point P is acted on by three forces; in the direction PA we have the surface tension σ_A of the liquid A against the gas space; in the direction PB the surface tension σ_B of the pure liquid B; in the direction PC the interfacial tension of A and B, σ_{AB}. Let us assume first of all that the liquids in equilibrium are completely miscible, and therefore that σ_{AB}, as a dynamic tension which tends to become zero, is very small. Then the liquid B will spread over the liquid A, if $\sigma_A > \sigma_B$. Experiment completely confirms the rule that, *of two completely miscible liquids, the one with the smaller surface tension spreads over that with the greater.* The conclusion may therefore be drawn from the spreading phenomena alone as to which

of two completely miscible liquids has the greater surface tension. Even very small differences in σ can be detected in this way; for a warmer liquid spreads over a colder one which is chemically identical.

If σ_{AB} has a finite value, if the liquids are therefore not completely miscible, then various possibilities exist.[1] Suppose that $\sigma_A > \sigma_B$, but that σ_{AB} is large in one case, small in the other. In order that B may spread upon A, we must have, according to Fig. 17,

$$\sigma_A > \sigma_B + \sigma_{AB} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If σ_{AB} is fairly large, then the case may arise that σ_A is not sensibly larger, or is even smaller, than $\sigma_B + \sigma_{AB}$. For we must further consider that σ_A and σ_B do not remain unchanged; B dissolves in A and vice versa. Further, according to the argument on p. 53, the altered static tension of A, σ_A', would be smaller than σ_A, while σ_B' would more likely be larger than σ_B; and even when B dissolves too little or too slowly in A to lower its surface tension quickly, we may suppose that vapour of B (say benzene) is quickly adsorbed upon the surface of A (water) and lowers the tension on account of the alteration in the surface-layer. Then the condition

$$\sigma_A' \leqq \sigma_B' + \sigma_{AB}$$

may be fulfilled. In this case the first drops of B do not need to spread out upon A; the vapour of B, or the first traces of the liquid, suffice to lower σ_A to σ_A', and the remainder of the liquid remains resting on the surface in lenticular form. This case actually occurs, especially when σ_{AB} is fairly large; e.g. in the case of water—petroleum, water—benzene, water—chloroform, and others (cf. Table 30, p. 87).

If on the other hand σ_{AB} is very small, as in the case of liquids which are largely miscible with one another, we observe the following: the first drop of B spreads out upon A, because

$$\sigma_A > \sigma_B + \sigma_{AB}.$$

It does not suffice, however, to saturate A with B, and to lower σ_A so far to σ_A', that a further drop of B does not spread, since still

$$\sigma_A' > \sigma_B + \sigma_{AB}.$$

The same may be the case with many further drops, and does not stop until A is covered with a layer of B. This case is found in pairs of liquids with a small σ_{AB}, such as water—ethyl ether, water—oil of turpentine, water—linseed oil, and others.

Everything that lowers σ_{AB} also favours spreading. Such a condition is the presence of dissolved substances, which strongly depress σ_{AB}. While, for instance, pure petroleum with a $\sigma_{AB} = 48{\cdot}3$ rests lenticularly upon water, petroleum containing mastic, with $\sigma_{AB} = 16{\cdot}3$, spreads rapidly.[2]

This is particularly true of substances which are soluble in B and lower the tensions σ_B and σ_{AB}. In the case of such dissolved substances, which are also soluble in A, and depress the tension σ_A, the formation of lenticular drops of B upon A is favoured. If for example we have an oil containing some fatty acid, and place a drop of it upon water, then the fatty acid will spread first; for both its σ_B, and particularly its σ_{AB}, are smaller than the σ_B and

[1] See on this point especially the investigations of *A. Pockels* [Nature, **43**, 437 (1891); **46**, 418 (1892); **48**, 152 (1893); **50**, 223 (1894); Wied. Ann. **67**, 668 (1899); Ann. d. Physik (4), **8**, 854 (1902); Phys. Zeitschr. **17**, 142, 441 (1916); Die Naturwiss. **5**, 137, 149 (1917)]; further also *Hardy* [Proc. Roy. Soc. London, **86**, A. 610 (1912); **88**, A, 303, 313 (1913)].

[2] *Pockels*, Wied. Ann. **67**, 668 (1899).

σ_{AB} respectively of the oil. The resulting fatty acid layer on the surface of the water lowers its surface tension to such an extent that the remainder of the oil does not spread, because σ_A' is no longer greater than $\sigma_B + \sigma_{AB}$. It is even possible that at the surface a hydrolytic decomposition of the oil is favoured—since the fatty acid so strongly depresses the surface tension, and, as will be discussed later (p. 139), the surface tension strives to displace a chemical equilibrium in such a sense as to favour the formation of capillary-active substances—so that we observe the phenomenon just described even with an oil originally free from fatty acid, as a consequence of the formation of traces of the latter.

The same is true when the surface of A was originally contaminated by traces of a surface-active substance ; for then σ_A is from the commencement so small that it does not overcome $\sigma_B + \sigma_{AB}$. Hence under certain circumstances it is a test of the cleanliness of a surface, for example of mercury, that a drop of another liquid spreads over it.

Again and again we find these processes becoming complicated in their nature from the fact that the speed with which the interfacial tensions are formed is very various. The following example [1] may be given. Pure hydrocarbons rest lenticularly upon water, also pure oils, the latter because an adsorption layer is formed. A solution of oils in petroleum, on the other hand, spreads at first and then breaks up into lenticular spots. This depends upon the fact that firstly the solution has a smaller interfacial tension σ_{AB} than the pure liquid, and then further that the surface tension σ_A is not lowered so quickly to σ_A' ; the drop therefore spreads at first, since

$$\sigma_A > \sigma_B + \sigma_{AB},$$

and only when σ_A' has been reached does the layer break up into drops, since

$$\sigma_A' \leqq \sigma_B + \sigma_{AB}.$$

Whether or not an adsorption layer spreads out from the drop when laid upon the surface may be seen from the phenomena of motion upon the surface. In order to detect them, the surface is dusted with a pure surface-inactive powder (ignited carbon, talc, and the like). If an adsorption layer is formed from the drop, the surface tension is depressed for a considerable distance around and the powder pushed back, since it is drawn from these places of lower surface tension to more distant points of higher tension. This phenomenon is not present when no adsorption layer is formed.[2]

We have therefore to distinguish the following cases :

1. Spread of liquid B upon liquid A, because σ_{AB} (and σ_B) is very small ; e.g. ether on water, or a petroleum containing mastic on water.

2. Lenticular drops of B upon A, because σ_{AB} is great, without σ_A being necessarily small. No formation of an adsorption layer, no " solution current " ; e.g. a pure petroleum hydrocarbon on water.

3. Lenticular drops of B upon A, mainly because σ_A' is small ; formation of an adsorption layer, " solution current," e.g. benzene on water, fatty acids on water, oils containing fatty acids and hydrocarbons on water, and others.

[1] *Pockels*, Physik. Zeitschr. **17**, 143–144 (1916).

[2] We frequently find the term " solution current " used for this kinetic phenomenon ; and for the altered surface, contaminated by an adsorption layer, the term " anomalous surface."

The question now arises, Is, in the case of a drop resting lenticularly upon a liquid, an equilibrium

$$\sigma_A' = \sigma_B' + \sigma_{AB}$$

really present, that is to say, is the direction in which $\sigma_B' + \sigma_{AB}$ acts opposite to that of σ_A', but situated upon the same straight line, or do the two liquids meet at a finite angle, the cosine of which would then enter into the formula? As a matter of fact, the angle of contact appears to be in many cases practically zero, for within the limits of error it is found that

$$\sigma_{AB} = \sigma_A' - \sigma_B' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

on condition that care is taken that the equilibrium tensions σ_A' and σ_B', and not σ_A and σ_B, are put into the equation. This condition appears to have been sufficiently fulfilled only by Antonow [1] among previous observers, and it is by no means easily fulfilled. Thus, the above-named investigator found in the case of water saturated with chloroform, without special precautions, a σ_A' of 61 to 64 dyne/cm.; but if the liquid was forced into the experimental pipette by air which had passed through a mixture of chloroform and water, and so was saturated with chloroform vapour, a value of 54·0 dyne/cm. was obtained.

In the following table, which is given from Antonow's results for the purpose of testing this formula, σ_A' always refers to water, σ_B' always to the other liquid. We can therefore in many cases calculate the boundary tension from the equilibrium tensions, but not from the surface tensions of the *pure* liquids.

TABLE 34

Relation of the Interfacial Tension σ_{AB} to the Surface Tensions σ_A' and σ_B'

Pair of Liquids.	σ_A'.	σ_B'.	$\sigma_{AB} = \sigma_A' - \sigma_B'$.	σ_{AB} (obs.).
Water—benzene (room temp.) .	60·0	28·2	31·8	32·6
Water—isobutyl alcohol (18°) .	23·9	22·5	1·4	1·76
Water—isoamyl alcohol (20°). .	25·7	21·1	4·6	4·4
Water—ethyl ether (14°) . . .	26·7	17·3	9·4	9·12
Water—chloroform (room temp.)	54·0	26·6	27·4	27·7

The behaviour of liquids at their critical point of mixture is noteworthy. There $\sigma_{AB} = 0$, hence from the above equation $\sigma_A' = \sigma_B'$. But the experiments of Whatmough [2] showed—and the experiments of Antonow [3] confirmed the result—that the surface tensions of the two layers already approximate closely at a temperature sensibly distant from the critical point of mixture. σ_{AB} therefore approached the zero value quite gradually; that is to say, not σ_{AB} alone is zero at the critical point of mixture, but also

$$\frac{d\sigma_{AB}}{dt} = 0.$$

This was quite to be expected. According to the theory of van der Waals (cf. p. 29), at the critical temperature of a liquid not only the surface tension, but also its differential coefficient with respect to temperature, are zero; it is therefore quite intelligible that the interfacial tension and its

[1] *loc. cit.* p. 86; see also *A. Pockels*, Wied. Ann. **67**, 668 (1899).
[2] *loc. cit.* p. 22. [3] J. Chim. Phys. **5**, 364 (1907).

differential coefficient with regard to temperature behave similarly at the critical point of mixture of two liquids.

In Fig. 18 the σ, t curves for the two phases of a mixture of water and isobutyric acid are plotted from Whatmough's experiments, curve 1 referring to the aqueous, and curve 2 to the isobutyric acid phase. We recognize how they touch, unite at the critical point of mixture (about 24°) and pass over into the σ, t curve for the single-phase solution above 25°.

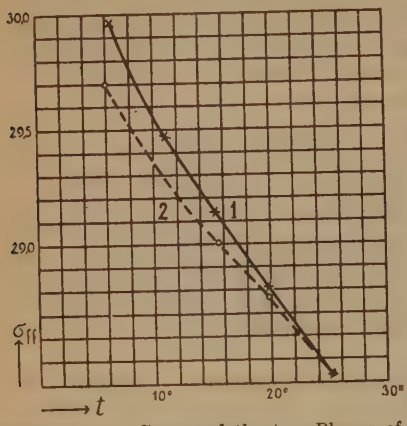


Fig. 18.—σ, t Curves of the two Phases of a Mixture of Liquids.

It might at first appear somewhat strange that two phases of such different composition as, say, water and isobutyric acid at 15° (18·2 per cent. isobutyric acid in the water phase, 62·59 per cent. in the isobutyric acid phase) should have surface tensions differing so little from one another (29·1 and 29·0 dyne/cm. respectively; see Fig. 18). This becomes comprehensible when we compare the σ, c curves for aqueous isobutyric acid solutions at 26·2° and 22°, as represented in Fig. 19A and B from Antonow's [1] experiments. The critical range falls in the horizontal part of the curve, in which the tension changes but slightly with the concentration.

It has sometimes been stated that if two liquids dissolve one another completely at the critical point of mixture, their interface becomes infinitely

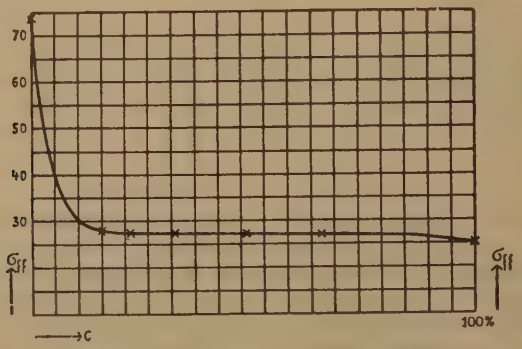


Fig. 19A.—σc, c Curve of Aqueous Isobutyric Acid Solutions at 26·2°.

large; and the possibility has been thought of that the interfacial tension may go through zero to negative values, and that this negative tension may cause the increase in surface, that is to say, the complete dissolution. This picture does not appear of value, however; for dissolution is not a surface phenomenon; we do not get a corrugation, as it were, of the interface with the production of an infinite surface. A process of quite another kind, namely, the diffusion caused by the thermal agitation of the molecules,

[1] *loc. cit.* p. 99.

causes the mutual dissolution of the two liquids, before the critical point of mixture is reached, and with continued existence of a positive interfacial tension. At the critical point of mixture a positive dynamic interfacial tension is at first present, until the mutual dissolution has been completed.[1]

If we have solutions of a third substance, equation (2) shows that various possibilities may be present. The interfacial tension σ_{AB} runs symbatic with the surface tension σ_A' (which may not without further question be put equal to σ_A, the surface tension of the pure liquid) if σ_B' is little altered by the third substance. As already remarked on p. 89, it is for this reason probable that substances which give surface-active solutions in water give also surface-active solutions against mercury, since they do not dissolve in mercury and change its σ towards air. If on the contrary σ_{AB} remains largely unchanged by the presence of the third body, then σ_B' must change greatly with σ_A'; that is, the third substance will dissolve in the second liquid and influence its tension against air. According to the observations of Bubanovič (cf. p. 89), ethyl alcohol, benzene,

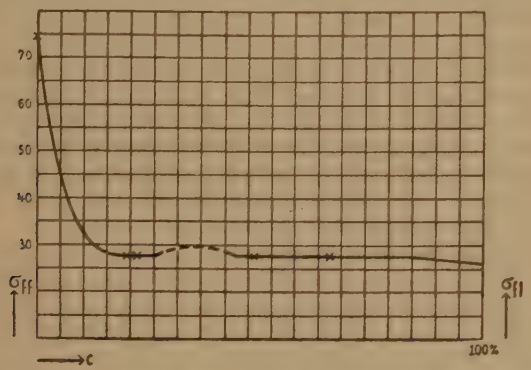


Fig. 19b.—σ_ϕ, c Curve of Aqueous Isobutyric Acid Solutions at 22°.

and other substances in the system water—olive oil, must belong to this class of third substances. With what has been said the fundamental rules are given, according to which we can predict how far a dissolved substance will act in the same direction upon the surface tension and upon the interfacial tension of a liquid.

Occasionally a drop of a liquid, when brought on to a liquid surface, exhibits the phenomenon of gliding about upon the surface for some time before it is taken up. This is often observed during titration, or also when, in rowing, water is splashed from the blades of the oars. According to Gossart [2] this is due, as in the case of the spheroidal state, to a thin layer of vapour or air, which holds the drop separated from the liquid surface. This can easily happen, since according to Poiseuille's Law, the velocity of efflux (see formula (1), p. 84) from capillary spaces is proportional to the

[1] See on this point particularly *Donnan*, Zeitschr. f. Physik. Chemie, **46**, 197 (1903). What has been said may also be advanced against the view of a negative boundary tension suggested by *Wo. Ostwald* [Grundriss der Kolloidchemie, 2 Aufl., Dresden, 1911, p. 80 et seq.] and *Tolman* [Journ. Amer. Chem. Soc. **35**, 317 (1913)].

[2] Ann. de chim. et de phys. (5), **4**, 391 (1895).

fourth power of the radius; the last thin layer of gas is therefore broken through comparatively slowly. Gossart found that in general a drop of a liquid will only glide about the surface of a liquid entirely like itself; this never happened when the drop and the liquid surface were chemically different. This is explained by the fact that in the case of chemical equality the liquid surface cannot dissolve away the layer of vapour surrounding the drop, while this is the case when a chemical difference is present. Also in the case of solutions, the gliding of drops is said only to occur in case of close similarity in composition. It is said that the content of a solution may be approximately determined by allowing it to fall in drops on to a liquid of similar composition, and altering the content of the latter until the drops glide easily.

III. The Interface Solid—Gas

The Surface Tension Solid—Gas

In the case of solid substances we have in general to make the distinction between amorphous and crystalline. The *amorphous solid* may be regarded as an undercooled liquid; its smallest particles are molecules which are arranged irregularly and not in a space lattice, and the relative motion of which is hindered by great internal friction. The same reasons hold for the existence of a surface tension as in the case of ordinary liquids. The same or similar methods may be applied for its determination as described earlier, provided that the viscosity of the amorphous substance in question allows of their application. Ignatiew [1] measured the σ of pitch from the size of drops (see p. 17), and found it to be about 30 dyne/cm.

Berggren [2] made use of a noteworthy method. A vertical thread of glass, pitch, or the like strives to become longer owing to the action of gravity, while the surface tension strives to shorten it. Its rate of deformation—change of length per unit of length and time—depends therefore chiefly upon the surface tension, along with influences due to viscosity and elastic forces. We have a characteristic limiting case in which the shortening due to surface tension is exactly balanced by the lengthening due to gravity, so that the length of the thread remains unchanged. For the interaction between surface tension and gravity we then have an argument similar to that applied in the deduction of the relation between surface tension and capillary rise (see p. 18), and we get the formula

$$\sigma = \tfrac{1}{2} r l \varrho g.$$

Here l is the length, which has been found by suitable shortening of the thread, r the radius of the cylindrical thread, and ϱ its density, g the acceleration due to gravity. Other limiting cases also allow the determination of the surface tension while dispensing with the measurement of viscosity. They are in part uncertain on account of the influence of elastic after-effects. In the case of pitch Berggren found a value of about 50 dyne/cm. at 18–20°; for a lead glass (French platinum glass) with a density of 3·94 at 17°, 70 dyne/cm. at about 500°. Resin and copal were also investigated. It appears to follow from these observations that within the possible range of

[1] Journ. Russ. Phys. Chem. Soc. **44**, 71 (1912): cited from Beiblätter d. Ann. d. Physik. **37**, 24 (1913).

[2] Ann. d. Physik (4), **43**, 61 (1914).

measurement the surface tension of amorphous solids is of the same order of magnitude as that of liquids.

Matters are less simple in the case of crystalline substances. The nature of the crystal state has been largely ascertained by means of the interference of X-rays. According to these results, as already remarked, the smallest particles of a crystal—at any rate in the case of heteropolar substances—are in general not molecules, but atoms or groups of atoms, which occupy the points of a space-lattice, and oscillate about these as equilibrium positions. A crystal has not minimum surface. Solidity is supreme to such an extent that in the case of a regularly formed crystal the atoms or groups of atoms occupy up to its extreme limits the positions required by the space-lattice, and no displacement in favour of a diminution of surface takes place. At the limit, however, the attractive forces of the atoms or atomic groups respectively of the crystal, which take part in the internal structure, will not be saturated, but will extend into the gas space; so that immediately at the boundary surface in the gas space a gradient of force will exist, as at the surface of a liquid. The potential energy of this boundary layer must strive towards a minimum, which tendency will show itself in all phenomena, where it is not prevented by rigidity. This boundary layer will also strive to become as small as possible, and small crystals will therefore have a higher vapour pressure than large ones, and will tend to increase in size by distillation. The formula deduced on p. 45 for small drops will therefore hold; one could therefore determine the surface tension of a solid substance, if one could measure the increase in vapour pressure of small crystals. The potential energy at the surface of a crystal will be distinguished from that at the surface of a liquid by the fact that it will be of different magnitude at the various characteristic crystal faces.

A large number of experimental results go to show that small crystals actually tend to pass over into large ones by distillation. If we generate in an exhausted vessel a fine deposit of sulphur or sulphur trioxide crystals, they unite to form a single large one after weeks or months. On passing air through finely powdered *p*-dichlorobenzene, F. W. Küster [1] found at first a higher vapour pressure than after some time, since the finest crystals had united to form coarser ones. Similar experiments were carried out by Pawlow [2] for a series of organic substances such as menthol, salol, azoxyphenetole, and others. However, as Meissner [3] emphasizes, such experiments cannot be regarded as conclusive, unless greater care is taken than hitherto with regard to constancy of temperature.

From the greater vapour pressure of smaller crystals it follows, as may be deduced thermodynamically, that the melting-point of a small crystal must be lower than that of a large one. This relation was first developed by F. W. Küster,[4] and then discussed and tested by Pawlow [5] in more

[1] Lehrb. d. allg. physik. u. theoret. Chemie, 1906, p. 187.

[2] Zeitschr. f. physik. Chemie, **68**, 316 (1910); see also e.g. *Ostwald*, Lehrb. d. allg. Chemie, **2** (3), 89, 1906.

[3] Zeitschr. f. anorg. u. allg. Chemie, **110**, 169 (1920).

[4] Lehrb. d. allg. physik. u. theoret. Chemie, 1906, p. 189.

[5] Zeitschr. f. physik Chemie, **65**, 1, 545 (1909); **74**, 562 (1910); also for the essential theoretical work, ibid. **75**, 48 (1911) and **76**, 450 (1911). With regard to the influence of the surface tension of a solid substance on the latent heat of fusion, see further *Girtler, loc. cit.*, p. 46.

detail. His experiments, according to Tammann [1] and Meissner,[2] will not bear critical examination. In the first place, he does not take into consideration that in the case of an artificially powdered solid the surface is far from defined and cannot therefore be trustworthily calculated. Then his experimental conditions were not of a kind to allow of his observing such a depression of the melting-point. Meissner, in similar experiments, used a beautiful method proposed by Tammann.[3] In this the melting of a fine crystal lamella, which was contained in a wedge-shaped space between a plane metal plate and a cylindrical lens, was followed. A temperature gradient was generated along the metallic plate in a direction parallel to the axis of the cylindrical lens. The isothermals were therefore at right-angles to this axis, and hence at right-angles to the edge of the wedge-shaped space. The line of melting, that is the limit between melt and crystal, ought to have been on an isothermal, if two circumstances had not caused a distortion. Firstly, only the metal was heated. Hence a current of heat goes through the melt at right-angles to the plate, and this results in the heat-current advancing more quickly, where the crystal lamella is thinnest, that is, where the cylindrical lens touches the plate. This therefore only causes the line of melting to form an obtuse angle with the direction of the temperature gradient, while remaining straight. But if the line of melting does not remain straight, but is bent forward at the narrowest point of the wedge in the direction of the temperature gradient, then this can only mean that the thinnest parts of the lamella melt at a lower temperature. A forward bend of this kind was observed in the case of azobenzene, myristic acid, and tristearin. We get the following equation for the lowering of the melting-point in such a thin film.

$$\sigma_s - \sigma_f = \Delta \frac{s \cdot \varrho}{2T_0} \frac{d_1 \cdot d_2}{d_1 - d_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here σ_s is the surface tension of the crystal, σ_f that of the liquid, T_0, s and r are melting-point, latent heat of fusion, and density of the crystal, d_1 and d_2 the thickness of the crystal lamella at two different points of the wedge-shaped space, between which there is a difference of temperature Δ. Meissner's experiments gave for the three substances named a value of $\sigma_s - \sigma_f$ of about 60 dyne/cm. The surface tension of the solid was therefore greater by this amount than the surface tension of the liquid. The thickness of the lamella at which the forward bend, and therefore the lowering of the melting-point, became apparent, was about 0·8 μ.

A further consequence of the rise in vapour tension with increased curvature of the surface should be the phenomenon observed by Reboul [4] that small ellipsoids of copper in a very dilute atmosphere of chlorine, iodine, and the like are attacked most quickly at the ends, that is, where the curvature is sharpest.

In other cases it appears necessary to ascribe the melting of small crystals directly to the surface tension, and not indirectly to the raising of the vapour pressure by the sharp curvature. Chapman and Porter [5] observed that a gold-leaf contracts from a certain temperature onwards (in their experiments 340°) instead of expanding upon heating. They explain

[1] Zeitschr. f. anorg. u. allg. Chemie, **110**, 166 (1920).
[2] *loc. cit.* p. 103.
[3] *loc. cit.* under [1].
[4] Compt. rend. **155**, 1227 (1912); **156**, 548, 688, 1376 (1913).
[5] Proc. Roy. Soc. A, **83**, 65 (1909); see also *Th. Turner*, Proc. Roy. Soc., A, **81**, 301 (1908).

this as follows. As the temperature rises the mechanical strength possibly decreases faster than the surface tension; the latter may therefore overcome the former above a certain temperature and cause a shrinkage of the leaf. Every stretched crystallite of the leaf behaves like the threads of amorphous material in Berggren's experiments.

Tammann [1] has developed the theory of these relations between strength and surface tension of metallic lamellæ in further detail, and Schottky,[2] on the basis of these considerations, attempted to estimate the surface tension of silver lamellæ from measurements of their tensile strength and temperature of shrinkage. This can only be done very roughly at present, for a metallic lamella of this kind is in reality a packet of lamellæ, and one measures the sum of the effects of the tensions of the single lamellæ.

Tammann [3] quite correctly explains so-called recrystallization by means of these shrinkage processes, and hence upon the basis of the surface tension solid—gas. Under the term recrystallization we understand the phenomenon that the crystallites first separating from a molten mass, which are generally very small, are able at many degrees below the melting-point to change gradually into coarser crystals. It is improbable that this increase in size depends solely upon a redistillation due to the higher vapour pressure of the smaller crystals: it is much more probable that the surface tension acts directly. In the range of temperature in question, and on account of the delicacy of the single lamellæ, it is able to overcome the mechanical strength and effect the union of small crystals to form larger ones. If the surface tension preponderates, then the crystal cannot be built to its furthest limits strictly according to the space-lattice, but corners and edges must round themselves off under the influence of the surface tension. In agreement with this, Tammann [4] emphasizes the fact that recrystallization has been particularly observed in the case of rounded crystallites. Also Gürtler's [5] "Einformung" is probably nothing but a recrystallization.

A further example of this behaviour, in which particularly the circumstance makes itself felt that the smallness of the particles especially favours the melting, is the fact that the smallest particles of corundum, etc., which can only be separated from the coarser by suspension in colloidal solution, sinter together at lower temperatures than coarser. This renders possible the manufacture of formed articles which cannot be made from coarser particles.[6]

Born and O. Stern [7] have attempted to calculate the surface tension

[1] *Nernst*-Festschrift, p. 428 (1912).
[2] *Nernst*-Festschrift, p. 437 (1912).
[3] *Nernst*-Festschrift, p. 428 (1912).
[4] *Nernst*-Festschrift, p. 434. See also the changed appearance of a tantalum wire which has been heated for 1,000 hours to 1,700° (*Küster* and *Thiel*, Lehrb. d. allg. physik. u. theoret. Chemie, 1913, p. 188).
[5] Zeitschr. f. physik. Chemie, **74**, 428 (1910). The difference between natural meteorites and ordinary iron-nickel alloys would be then explained by recrystallization.
[6] D.R.P. Nr. 292,334. It is, however, questionable whether the increase of size of the particles in sintering depends upon the tension solid—gas or upon the tension solid—liquid; for in the case of many, if not all, sintering processes, the presence of a more easily fusible impurity is important, and we should then be dealing with the boundary tension of the solid against this melt [cf. *Endell*, Silikat-Zeitschr. **2**, Heft 1 and 2 (1914)].
[7] Sitzb. d. Berl. Akad. d. Wiss. **48**, 901 (1919).

of crystals of the alkaline halides upon the basis of the electrical space-lattice theory of heteropolar crystals.[1] To these halides a very simple structure may be ascribed; in a cubical space-lattice, the points of the lattice are occupied alternately by the ions of the alkaline halide. The surface tension may be calculated by means of the following simple argument. If we imagine a crystal cut by a plane, then the surface work necessary to generate the two new surfaces (at absolute zero) is equal to the potential energy which originally held together the parts of the uncut crystal. This potential energy can be determined from the electrical attractive forces between the ions of the crystal and its grating-constant, that is, the distance between ions of like kind; in this way we get

$$\sigma = \frac{0{\cdot}1166\epsilon F}{4} \frac{\varrho}{A_1 + A_2}.$$

Here ϵ is the charge of the electron, F the electro-chemical constant (96,540 coulombs), ϱ the density of the salt, A_1 and A_2 the atomic weights of the elements of which it is composed. The values thus found are, however, somewhat lower than we might expect; e.g. for KI a value of 74·9 dyne/cm. is obtained, whereas F. M. Jaeger[2] found even at 737° a value 75·2, and the same is true for the other Na and K halides. But it must be remembered that the argument is still of an entirely approximate kind.[3]

General Remarks upon the Adsorption of Gases at Solid Surfaces

At the interface liquid—gas, the great relative mobility of the liquid particles makes the measurement of the surface tension easy, but it renders difficult the measurement of the amount adsorbed; the $\frac{d\sigma}{dc}$ of Gibbs's formula is easily determined, a on the other hand with difficulty. At the interface solid—gas matters are reversed; the rigidity of solid substances makes it possible that a comparatively small amount of substance should develop a very large surface, which remains unchanged; this ensures large amounts of adsorbed material which do not change and are easily measurable. On the other hand, as already mentioned, the surface tension can hardly be determined with certainty on account of the rigidity; hence we can easily measure a, but $\frac{d\sigma}{dc}$ only with difficulty.

Extremely porous substances, such as wood-charcoal, meerschaum, etc., have long been known, which certainly have a highly developed boundary surface against the gas space, and it has long been known that they are able to take up in loose combination amounts of gas. After Scheele and Fontana,[4] who were the first to describe the phenomenon, de Saussure[5] already in 1814 subjected it to detailed investigation. Among later investigations, those of Chappuis,[6] Joulin,[7] and Kayser,[8] and the recent

[1] *Born* and *Landé*, Verh. d. deutsch. physik. Ges. **20**, 210 (1918); *Born*, Verh. d. deutsch. physik. Ges. **21**, 13, 533 (1919). See also *Born*, Z. für Phys. **7**, 217 (1921).

[2] Koninkl. Akad. v. Wetensch. Amsterdam, **17**, 563 (1914).

[3] Attention may be drawn to some very recent papers bearing on the foregoing section: *Polanyi*, Z. für Phys. **7**, 325 (1921); *Carpenter* and *Miss Elam*, Phil. Trans. **100**, 329 (1921). [Trans.]

[4] For the older literature see *Ostwald*, Lehrb. d. allg. Chemie, 1st. Ed., Vol. I, p. 778 (1884). Further also *Chappuis*, Wied. Ann. **8**, 1 (1879).

[5] Gilb. Ann. **47**, 113 (1814).

[6] Wied. Ann. **8**, 1 (1879); **12**, 161 (1881); **19**, 21 (1883).

[7] Ann. de chim. et de phys. (5), **22**, 397 (1881).

[8] Wied. Ann. **12**, 526 (1881); **14**, 450 (1881).

work of Titoff [1] and Miss Homfray [2] deserve special mention. Dewar [3] made use of the strong adsorptive power for gases and vapours of cocoanut charcoal at low temperatures for the production of high vacua. This and the widespread use of charcoal for the air-filters of gas-masks during the war have made the phenomenon generally known.

It may now be taken as certain that in a large number of cases this condensation of a gas by a porous solid is a pure adsorption; a surface condensation as required by Gibbs's formula. Often, however, this does not occur alone, but is accompanied by an actual chemical reaction or the solution of the gas in the mass of the solid. The problem thus often arises of differentiating the adsorption from these other processes.

The porous solid structures such as wood, charcoal, etc., which will be considered below, belong actually to the sphere of colloid chemistry, for they are disperse systems, solid foams, as they were termed in the divisions on page 3. But we cannot avoid dealing with them in advance at this point, since the whole science of the adsorption of gases and solutions is bound up with these structures on account of the magnitude of the measurable adsorption.

In the following we are dealing for the present exclusively with the adsorption of a simple pure gas, and further, generally with that of a true gas, not a vapour in the neighbourhood of its saturation-point.

The Velocity of Adsorption at the Interface Solid—Gas

Theoretically it is to be expected that the velocity of adsorption at the interface solid—gas should be great (cf. p. 50). The gas molecules which are in the range of attraction of the solid surface will be very quickly condensed upon it. Into this depleted space the gas molecules diffuse from outside. Since the adsorbing solid, the *adsorbent*, is generally a solid foam, and hence has an internal surface, which is possibly only accessible to the gas, the *adsorbed substance*, through comparatively long and narrow pores, considerably longer times are required for the adsorption by means of charcoal, meerschaum, and the like than for the small interfaces in the case of liquids, as referred to on p. 52. The adsorption equilibrium is mostly reached in several seconds or minutes.

The following arrangement is convenient for the measurement of the velocity of adsorption. A weighed amount of adsorbent is sealed into an evacuated, thin-walled glass vessel. This vessel is brought into a wide glass tube, which can be rotated about its axis, and contains the gas to be investigated. By turning the tube about its axis, the vessel inside is caused to break. This may also be done from outside by means of a magnet. The error, which is caused by the initial streaming of the gas into the vacuum of the vessel, makes it necessary to assume a zero-point other than the moment of breaking the vessel for the time scale of the observed adsorption curve. It is often sufficient to leave the air in the vessel, and close the latter by means of a long open capillary, so that the pressure may equalize itself without the gas diffusing into the vessel. The wide tube communicates with a sensitive and quick-acting manometer. For this purpose a glass globe is suitable, over which a very thin glass plate or metallic mem-

[1] Zeitschr. f. physik. Chemie, **74**, 641 (1910).
[2] *Ibid.* **74**, 129, 687 (1910); also Proc. Roy. Soc. **84**, 99 (1910).
[3] Proc. Roy. Soc. **74**, 122 and 127 (1904).

brane is stretched, such as is used for the manufacture of aneroid barometers. This carries a mirror which reflects a ray of light on to a photographic plate moved with known speed. The reduction in pressure in the tube during adsorption is thus graphically recorded directly upon a photographic plate.

Instead of a revolving tube we may employ one of several metres in length set vertically, in which the vessel is shattered by a magnetic device from outside, and the adsorbent, in the form of as fine a powder as possible, made to fall down slowly through the tube.

Fig. 20 shows a curve of adsorption velocity of this sort, traced from the photographic record, and referring to the adsorption of carbon dioxide by an efficient technical adsorption charcoal. Equilibrium is attained in 20 seconds.

Bergter [1] has measured the velocity of adsorption of nitrogen and air by cocoanut charcoal; he followed the change of the volume with time by means of a liquid manometer. Giesen [2] determined the velocity of adsorp-

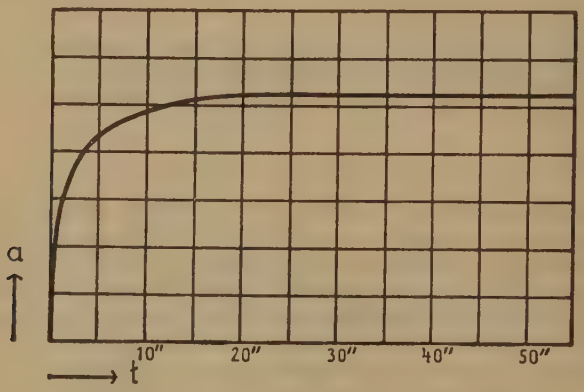


Fig. 20.—Curve of Velocity of Adsorption.

tion by measuring the increase in weight of an ignited piece of carbon in various gases (air, CO_2, NH_3), employing a Salvioni micro-balance. This method does not permit of the amounts taken up in the first few seconds being determined. The equilibria were found by him to be attained in 8 to 10 minutes. Harned [3] also measured the velocity of adsorption of some vapours on charcoal at very low pressures from the increase in weight of the charcoal.

All these measurements, as well as many older qualitative results (de Saussure,[4] Kayser,[5] Travers [6]), agree to the extent that adsorption equilibrium is reached very quickly, generally in a few minutes, in the case of chemically inert gases, in which no actual chemical interaction has to be reckoned with. The curves of adsorption velocity cannot be simply represented by a mathematical function. They rise very steeply and bend round sharply immediately before equilibrium is reached. Bertger points

[1] Ann. d. Physik (4), **37**, 472 (1912).
[2] *Ibid*, **10**, 838 (1903).
[3] Journ. Amer. Chem. Soc. **42**, 372 (1920).
[4] *loc. cit.* p. 106.
[5] *loc. cit.* p. 106.
[6] Proc. Roy. Soc. **A**, **78**, 9 (1906).

out that these sharply bent curves may be represented by the sum of two *e* functions. A simple course is also hardly to be expected; in the first place, we are dealing mainly with a diffusion under variable pressure gradient. Besides, the temperature conditions are only known inaccurately; the heat of adsorption is great, the adsorbent warms up strongly in the first few minutes, and the conditions for a quick escape of heat for the purpose of maintaining a steady temperature are unfavourable.

We may suppose with great probability that, if the condensation of a gas by an adsorbent does not lead quickly to equilibrium, we are not dealing with pure adsorption, but in addition with a solution of the gas in the interior of the solid or an ordinary chemical reaction between gas and adsorbent. It is well to follow McBain [1] in calling the whole phenomenon *sorption*. The pure surface condensation is *adsorption*, the solution in the interior of the solid *absorption*.

McBain was able to show that adsorption may very well be distinguished from absorption. When hydrogen is taken up by cocoanut charcoal at the temperature of liquid air, both phenomena appear to be present. The following experiments were made. Charcoal saturated with hydrogen was brought into a vacuum; the gas condensed upon the surface was immediately given up, that present in the interior diffused out slowly. If the pressure of the hydrogen in the gas space was increased, but not by so much as to bring it into equilibrium with the hydrogen in the interior of the carbon, a quick lowering of pressure first occurred on account of the adsorption on the surface and then a slow increase in pressure owing to hydrogen continuing to diffuse out from the interior.

The reverse experiment also succeeded. A charcoal as free from gas as possible was brought into an atmosphere of hydrogen, in which it adsorbed hydrogen; this process proceeded very quickly even at the temperature of liquid air. In two minutes about 99 per cent. of the amount to be taken up had been accounted for. The pressure was then lowered; the surface was therefore supersaturated with adsorbed gas, and accordingly gave some up, an increase of pressure being thus effected; then the pressure again diminished, as the diffusion of the hydrogen into the interior of the carbon made itself more and more felt. By sufficiently quick working, therefore, the adsorption equilibria may be made to set themselves up from both sides, independently of the concomitant slow absorption.

The taking-up of oxygen by charcoal is certainly a sorption, and, in fact, in addition to the adsorption we have to consider a pure chemical reaction between the two substances with formation of CO or CO_2 (for further information see p. 143).

According to Bergter the velocity of adsorption is not seriously influenced by the degree of fineness of the adsorbent. In his cases, however, he was dealing only with an increase of surface of about 30 per cent. In the case of the adsorption of CO_2 by films of celluloid [2] the velocity of adsorption increased sensibly the finer the films were, the greater, that is, the ratio of external surface to weight; it increased thirty-fold upon the ratio in question being increased five-fold.

[1] Phil. Mag. (6), **18**, 916 (1909); Zeitschr. f. physik. Chem., **68**, 471 (1909).

[2] *Lefebure*, Journ. Chem. Soc. **105**, 328 (1914). The taking-up of gas by celluloid has all the characteristics of an adsorption: the usual adsorption isothermal, negative temperature coefficient, relation between adsorbability and condensibility. The character of the curves of adsorption-velocity indicates that alongside the adsorption a solution takes place.

Adsorption-equilibrium at the Interface Solid—Gas. The Adsorption Isothermal

Adsorption equilibrium is measured as follows. A weighed amount of adsorbent is first freed by heating and evacuation from already adsorbed gases; the temperature is raised to over 500°,[1] and a vacuum of 0·001 mm. produced. After cooling a measured amount of gas is admitted, and, after waiting until no further gas is taken up, the pressure and volume of the gas are again determined. If increasing quantities of the gas are admitted one after the other, the dependence of the amount adsorbed upon the pressure may conveniently be determined, while the quantity and properties of the adsorbent remain unchanged. It is convenient to work in a room of constant temperature, or to immerse adsorption vessel and gas-burette in a thermostat.[2]

De Saussure [3] already convinced himself that a definite end state is reached, and obtained for the adsorption of different gases by means of a piece of meerschaum the same values upon repeating the experiments, although the meerschaum had been used in the interval for the adsorption of other gases. Joulin [4] expressly tested the question of equilibrium and showed that exactly the same final state is reached, whether we measure with rising or falling pressure, and this was frequently confirmed afterwards.[5] That a concomitant solution process in the interior of the adsorbent does not disturb the reversible establishment of the adsorption equilibrium was already shown on p. 109.

To each equilibrium pressure p there belongs a definite amount adsorbed. It would be in principle correct to refer this to 1 sq. cm. of surface. Since we have at present no method of determining the active surface of an adsorbent, which surface is for the most part an internal one, and hence only know its size in rare cases, there is no alternative but to refer the amount adsorbed to 1 gram of adsorbent. Hence we have the amount adsorbed $a = \frac{x}{m}$, where x is the total amount adsorbed and m the weight of adsorbent. In the following the pressure p will always be given in centimetres of mercury. a is the gas volume expressed in cubic centimetres and reduced to 0° and 760 mm. adsorbed by 1 gram of adsorbent.

In the case of the same adsorbent, assuming a sufficient uniformity, a is proportional to a', the amount adsorbed per square centimetre. a' is equal to the excess $\mathfrak{a}$ appearing in the Gibbs adsorption formula, increased by the small amount $\mathfrak{a}'$, which would be present in 1 sq. cm. of surface layer if no adsorption took place. Hence

$$a' = \mathfrak{a} + \mathfrak{a}'.$$

Now the surface-layer is so thin that at the usual small gas pressures $\mathfrak{a}'$ may be neglected as small compared with $\mathfrak{a}$, hence $a' = \mathfrak{a}$, and hence is also proportional to a.

[1] According to *Mohr* [Ann. d. Physik, **51**, 569 et seq. (1916)] charcoal must be heated to over 1,000° in order to free it completely from gas. That even at 800° charcoal sensibly adsorbs CO_2 appears from experiments by *Arndt* and *Schraube* [*Nernst*-Festschrift, p. 46 (1912)].

[2] For a different procedure see *Seeliger*, Zeitschr. f. Phys. **4**, 189 (1921); he determines the mass of gas adsorbed by measuring the period of torsional oscillation of the adsorbent before and after the adsorption.

[3] *loc. cit.* p. 106.

[4] *loc. cit.* p. 106.

[5] e.g. *Orme Masson* and *E. S. Richards*, Proc. Roy. Soc. **78**, A. 412 (1907).

The a, p curves are, as Fig. 21A shows, curved concave to the p axis. They are entirely similar to the curves in Figs. 16B and C, as described in the case of adsorption by drops of mercury in aqueous solution. A theoretically well-founded equation, giving the a, p curve over a considerable range, is not known. The empirical general parabolic equation

$$a = \alpha p^{\frac{1}{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which α and $\frac{1}{n}$ are constants, is still nearly always used. α is the *adsorption value*, the amount adsorbed at unit pressure, that is, at 1 cm. of mercury. It is characteristic for the adsorbent and the gas adsorbed. The *adsorption-exponent* $\frac{1}{n}$ lies between 0·2 and 1, and varies, as will be discussed later (cf. p. 120), in a regular manner with the temperature and the nature of the adsorbed gas. Formula (1) is referred to in the following pages as the *adsorption isothermal*. The validity of a formula of this kind can be tested by the fact, as already mentioned on p. 67, that it gives a straight line when logarithms are taken.

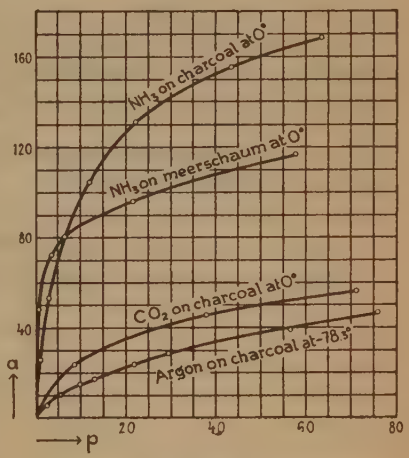


FIG. 21A.—Adsorption Isothermals of Various Gases.

$$\log_{10} a = \log_{10} \alpha + \frac{1}{n} \log_{10} p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(see Fig. 21B). Plotting in a logarithmic diagram allows of an easy calcu-

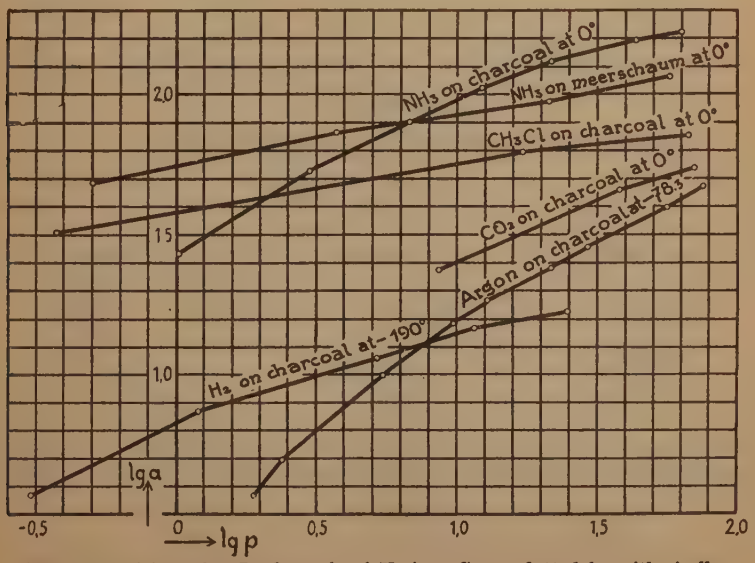


FIG. 21B.—Adsorption Isothermals of Various Gases plotted logarithmically.

lation of $\frac{1}{n}$. It is equal to the tangent of the angle of inclination of the log a, log p straight lines to the log p axis. The angle of inclination which the line joining every two experimental points makes with the log p axis is measured with a protractor, and the mean of the tangents is taken. The value of a is best determined by calculation, by introducing the value of $\frac{1}{n}$ found, calculating the a values, which are obtained by putting in the experimentally obtained a, p values, and then taking the mean.

Fig. 21B shows that the experimental values differ from the theoretical inasmuch as the log a, log p curves are slightly concave to the log p axis. At small pressures $\frac{1}{n}$ is near to 1, and declines with increase of pressure. How far the agreement between observation and calculation goes is shown by the following tables.

TABLE 35

The Adsorption of Argon by Cocoanut Charcoal at −78·3° [1]

$a = 3{\cdot}698\,;\ \frac{1}{n} = 0{\cdot}6024$

p (cm. of Mercury).	a (obs.).	a (calc.).
0·8	1·6	—
1·9	3·7	—
2·4	5·0	—
5·42	9·9	10·2
9·84	15·4	14·7
12·9	18·6	17·3
21·8	24·0	23·7
29·5	28·8	28·4
56·4	39·4	41·9
75·8	46·9	50·1

TABLE 36

The Adsorption of Ammonia by Meerschaum at 0° [2]

$a = 54{\cdot}83\,;\ \frac{1}{n} = 0{\cdot}184$

p (cm. of Mercury).	a (obs.).	a (calc.).
0·500	48·3	48·3
3·713	72·3	69·8
21·50	95·3	96·4
57·56	117	116

The example of argon is given with intent to show how improbable it is that adsorption is to be explained by chemical combination in the ordinary

[1] From experiments by *Miss Homfray, loc. cit.* p. 107.
[2] From experiments by *Chappuis, loc. cit.* p. 106.

sense, although the attractive force acting may finally be regarded as a chemical action.

The conditions for the action of the surface forces at all boundary surfaces are entirely similar, if we leave for the moment crystalline substances out of account. We are always dealing with a potential gradient which is caused by the molecular forces, acts only at a short distance from the interface, and is lowered as far as possible by a suitable distribution of the substance whose concentration can vary. It thus appears entirely permissible to apply the experience which has been gained concerning one interface to another. Hence the question suggests itself whether the course of the adsorption isothermal is in agreement with what we can deduce from the course of the σ, c curve and the Gibbs adsorption formula.

We might at first be tempted to take one of the empirical formulæ for the dependence of σ of capillary-active solutions upon the concentration, form the differential coefficient $\frac{d\sigma}{dc}$, introduce its value into the Gibbs adsorption formula, and test whether the adsorption isothermal appears. As a matter of fact we get it when we start from equation (6) on p. 66.

$$\frac{\sigma_M - \sigma_L}{\sigma_M} = \beta c^{\frac{1}{n}}.$$

Then

$$-\frac{d\sigma}{dc} = \frac{\sigma_M \cdot \beta}{n} c^{\frac{1}{n}-1},$$

and this introduced into the Gibbs adsorption formula

$$\mathfrak{a} = -\frac{c}{RT}\frac{d\sigma}{dc}$$

gives (remembering that $\mathfrak{a}$ is proportional to a)

$$a = \alpha c^{\frac{1}{n}}.$$

Hence, since p is also proportional to c,

$$a = \alpha p^{\frac{1}{n}}.$$

If we apply v. Szyszkowski's formula [1] in a similar manner,

$$\frac{\sigma_M - \sigma_L}{\sigma_M} = \mathfrak{b} \log\left(\frac{c}{\mathfrak{c}} + 1\right),$$

we get on differentiation

$$-\frac{d\sigma}{dc} = \mathfrak{b}\sigma_M \frac{1}{c + \mathfrak{c}}, \quad \ldots\ldots\ldots \quad (3)$$

and this, put into the Gibbs adsorption formula, taking the same proportionalities into account as before, gives

$$a = a_s \frac{p}{p + \mathfrak{c}},$$

where a_s is a constant.

This formula suffices for limiting cases. If p is small it may be neglected compared with $\mathfrak{c}$. Then a is proportional to p, that is to say, the adsorption exponent $\frac{1}{n}$ is equal to 1 for small pressures. Conversely, for large pressures, $\mathfrak{c}$ can be neglected in comparison with p. Then a is constant, that

[1] See *Langmuir*, Journ. Amer. Chem. Soc. **39**, 1885 (1917).

is, the quantity adsorbed approaches a state of *saturation*, which has hardly been strictly described for gases up to the present, but certainly for solutions (cf. p. 182). The middle bent part of the a, p curve is not well reproduced by the equation.

The course of the adsorption isothermal is therefore to a great extent the same as we should expect on the basis of the σ, c curve of capillary-active substances; the large adsorbed amounts at small pressures and concentrations correspond to the strong depression of σ at small concentrations.

The Dependence of Gas-adsorption upon the Temperature and the Nature of the Gas

The adsorption of a gas declines, as far as present experience goes, in general with rise of temperature. This is in agreement with the fact that

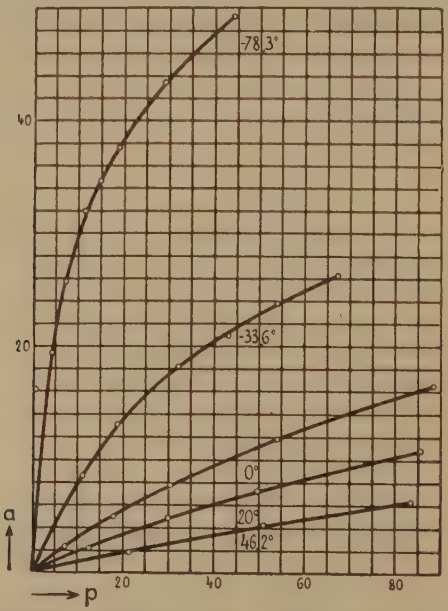


Fig. 22A.—Adsorption Isothermals of CO on Charcoal at Various Temperatures.

the surface tension decreases with rise of temperature, and that its variability caused by the presence of a second substance is in general smaller, the smaller the surface tension. Fig. 22A shows the adsorption isothermal of CO for various temperatures according to Miss Homfray's measurements.[1] The pressures are again in centimetres of mercury, the adsorbed amount in c.c. at 0° and 760 mm., referred to 1 gram of adsorbent. The logarithmic representation in Fig. 22B is still clearer. We see that the angle of inclination of the log a, log p straight lines increases with increase of temperature, and approaches the value 45°. The adsorption exponent hence approaches the value 1, rising from a small value at low temperatures. Attention may be further drawn to the fact that the greater $\frac{1}{n}$ is, the flatter is the bend of the

[1] *loc. cit.* p. 107.

a, p curve; the smaller $\frac{1}{n}$, the sharper is the bend and the lower the pressure

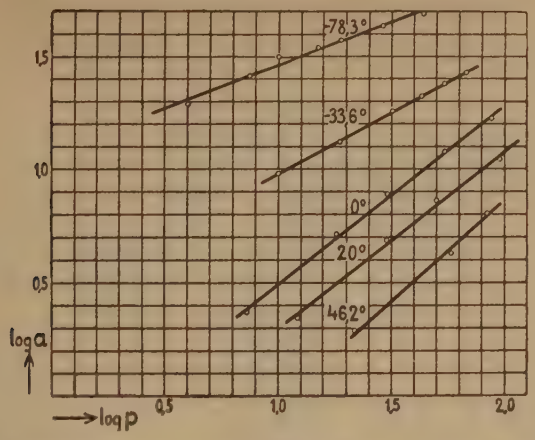


Fig. 22b.—Adsorption Isothermals of CO on Charcoal plotted logarithmically.

at which it occurs. In Fig. 23 curves are plotted according to the equation

$$a = \alpha p^{\frac{1}{n}}$$

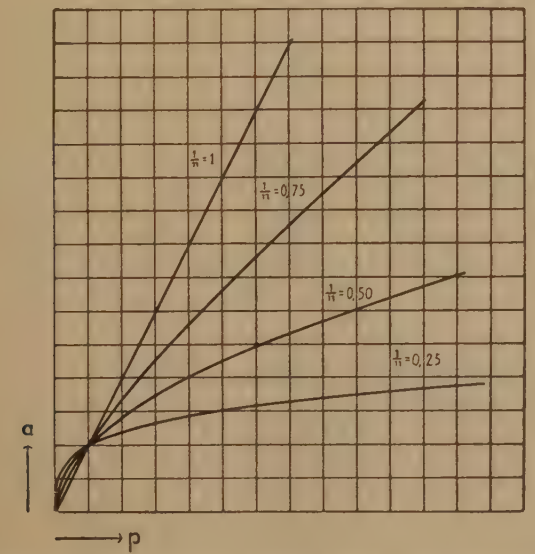


Fig. 23.—Adsorption Isothermals for Various Values of the Adsorption Exponent.

with equal α's, but different values of $\frac{1}{n}$, in order to make this behaviour clear. Tables 37 to 41 give the observed values of a and those calculated from the adsorption isothermals, and show the numerical decrease of adsorp-

tion value a, and the increase in the adsorption exponent $\frac{1}{n}$ with rise of temperature. Titoff [1] described this fan-shaped radiation of the log a, log p straight lines in the case of N_2, CO_2, and NH_3, and Miss Homfray also for CO, N_2, argon, methane, ethylene, and CO_2. Cocoanut charcoal was always the adsorbent.

TABLE 37

Adsorption of CO on Cocoanut Charcoal at − 78·5°

$$a = 11{\cdot}96\,;\ \frac{1}{n} = 0{\cdot}3839$$

p.	a (obs.).	a (calc.).
0·6	16·2	—
4·0	19·4	20·4
7·2	25·7	25·5
11·7	31·7	30·7
14·8	34·7	33·6
18·7	37·6	36·8
28·8	43·4	43·5
44·2	49·3	51·2

TABLE 38

Adsorption of CO on Cocoanut Charcoal at − 33·6°

$$a = 2{\cdot}514\,;\ \frac{1}{n} = 0{\cdot}5601$$

p.	a (obs.).	a (calc.).
10·1	8·54	9·18
18·8	13·1	13·0
32	18·2	17·5
43	21·0	20·7
54	23·8	23·5
67	26·3	26·5

TABLE 39

Adsorption of CO on Cocoanut Charcoal at 0°

$$a = 0{\cdot}5590\,;\ \frac{1}{n} = 0{\cdot}7605$$

p.	a (obs.).	a (calc.).
7·3	2·34	2·54
18·0	5·17	5·03
30·4	7·84	7·51
54·0	11·9	11·6
88·2	16·5	16·9

[1] *loc. cit.* p. 107. We also find it in the case of the adsorption of CO_2 by charcoal in the experiments of *Geddes* [Ann. d. Physik (4), **29**, 797 (1909)].

TABLE 40

Adsorption of CO on Cocoanut Charcoal at 20°

$$a = 0{\cdot}2872\,;\ \frac{1}{n} = 0{\cdot}8219.$$

p.	a (obs.).	a (calc.).
12·3	2·19	2·26
30·0	4·80	4·70
49·5	7·27	7·10
85·6	11·0	11·1

TABLE 41

Adsorption of CO on Cocoanut Charcoal at 46·2°

$$a = 0{\cdot}1508\,;\ \frac{1}{n} = 0{\cdot}8431$$

p.	a (obs.).	a (calc.).
21·4	1·94	1·99
50·9	4·22	4·14
83·5	6·34	6·29

There is a two-fold dependence upon temperature to be taken into account. In the first place we can keep p constant and compare the amounts adsorbed at different temperatures. The curves thus obtained are called by W. Ostwald *isobars*.[1] Or we consider *isosteres*, that is, we keep the amount adsorbed constant and compare the pressures at different temperatures. Fig. 22B shows that at constant p the $\log a$, $\log p$ straight lines cut off portions of the ordinate, which are to a considerable degree proportional to the temperature. Hence for a pressure p_1 the equation

$$\log_{10} a_t = \log_{10} a_0 - \zeta_1 t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

holds, where ζ is a constant. For a pressure p_2 the ζ_2 is different. The ζ values increase linearly with decrease of $\log p$; the straight lines spread out fan-wise. We have then in general for the isobars

$$\log_{10} a_t = \log_{10} a_0 - (\zeta - \xi \log_{10} p)t$$

$$a_t = a_0 e^{-(\zeta - \xi \log_{10} p)t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In order to test this equation, we deduce the $\log a$, t straight lines from the $\log a$, $\log p$ lines. These give the values of ζ_1, ζ_2, etc. From the ζ, $\log p$ lines we then get ζ and ξ. For the above-mentioned experiments of Miss Homfray with CO, for example, Table 42 was obtained.

[1] "Lehrb. d. allg. Chemie," II, 3, p. 226 (1906).

TABLE 42

Isobars of the Adsorption of CO on Cocoanut Charcoal for $p = 40$ cm. Hg.

$a_0 = 9{\cdot}46$; $\zeta = 0{\cdot}01515$; $\xi = 0{\cdot}003607$

Temp.	a_t (obs.).	a_t (calc.).
−78·3	51·2	48·0
−33·6	20·1	19·5
0	9·46	—
+20	6·07	6·14
+46·2	3·41	3·49

The meaning of ζ and ξ is obtained as follows. Since a is the value of a for $p = 1$, therefore

$$\log_{10} a_t = \log_{10} a_0 - \zeta t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

hence

$$\zeta = -\frac{d \log_{10} a_t}{dt} = -\frac{\log_{10} e}{a_t} \frac{da_t}{dt} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If, further, we differentiate the adsorption isothermal $a = \alpha p^{\frac{1}{n}}$ with respect to t we get

$$\frac{da}{dt} = p^{\frac{1}{n}} \frac{d\alpha}{dt} + \frac{\alpha}{n} p^{\frac{1}{n}-1} \frac{dp}{dt} + \alpha p^{\frac{1}{n}} \log p \frac{d\frac{1}{n}}{dt} \quad . \quad . \quad . \quad (5)$$

If we put for the isobars $\frac{dp}{dt} = 0$, we get

$$\frac{da}{dt} = p^{\frac{1}{n}} \frac{d\alpha}{dt} + \alpha p^{\frac{1}{n}} \log p \frac{d\frac{1}{n}}{dt}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and putting in now the value of $\frac{da}{dt}$ from equation (4) and $\log p = \frac{\log_{10} p}{\log_{10} e}$ we arrive at

$$\frac{da}{dt} = -a\left[\frac{\zeta}{\log_{10} e} - \frac{\log_{10} p \, d\frac{1}{n}}{\log_{10} e \, dt}\right].$$

If on the other hand we differentiate equation (2), keeping p constant, we find that

$$\frac{da}{dt} = -a\left[\frac{\zeta}{\log_{10} e} - \frac{\log_{10} p}{\log_{10} e} \xi\right] \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Hence

$$\xi = \frac{d\frac{1}{n}}{dt}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

It is also evident from Fig. 22B that the change in $\log_{10} a$ with temperatuer is composed of two parts, $\frac{d \log_{10} a}{dt}$, caused by the displacement, and $\log_{10} p . \frac{d\frac{1}{n}}{dt}$ caused by the rotation.

In order to deduce the equation of the isosteres, we must put $\frac{da}{dt} = 0$ in equation (5). We get

$$\frac{dp}{dt} = -\frac{np}{a}\frac{da}{dt} - np \log p \frac{d\frac{1}{n}}{dt} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

If we replace $\frac{da}{dt}$ by $-\frac{a\zeta}{\log_{10} e}$ according to equation (4), and again $\log p$ by $\frac{\log_{10} p}{\log_{10} e}$, and $\frac{d\frac{1}{n}}{dt}$ by ξ according to equation (8), and divide by p, we find

$$\frac{d \log_{10} p}{dt} = n(\zeta - \xi \log_{10} p) \quad . \quad . \quad . \quad . \quad . \quad (10)$$

While, as we can see from equation (7), $\frac{d \log_{10} a}{dt} = \text{const.}$, and the isobars referred to $\log_{10} a$ are therefore straight lines, $\frac{d \log_{10} p}{dt}$ according to equation (10) is not constant. It is the greater, the lower the temperature (then n is greater) and the smaller the pressure (then $\log_{10} p$ is negative). In agreement with this, the $\log_{10} p$, t curves rise at first steeply, to bend round later towards the t axis.

These considerations are only valid for not too high temperatures and pressures, that is, within the range in which the $\log_{10} a$, $\log_{10} p$ straight lines radiate fan-wise. At higher temperatures (and, as will be discussed immediately, from a temperature onwards which depends to some extent on the condensibility of the gas), $\frac{1}{n}$ becomes $= 1$, and it keeps this value at still higher temperatures. The $\frac{1}{n}$, t curve therefore is at low temperatures a straight line inclined at an angle whose tangent is ξ, then bends off fairly sharply, and runs further parallel to the t axis. ξ therefore becomes zero and we have for the equation of the isobars on the basis of equation (2)

$$\log_{10} a_t = \log_{10} a_0 - \zeta t.$$

For the isosteres (from equation 10)

$$\log_{10} p_t = \log_{10} p_0 - \zeta t.$$

As far as experiments go, ζ does not appear to change its value at high temperatures.

The measurements, particularly Miss Homfray's, allow of a comparison between the behaviour of different gases with the same adsorbent (cocoanut charcoal). We find in all cases the fan-like divergence of the $\log a$, $\log p$ lines above described. As Table 43 shows, the temperature coefficients

ζ and ξ vary comparatively little from gas to gas; that is, the amount by which the log a, log p line is displaced and turned as the temperature rises, is not greatly dependent upon the nature of the gas.

TABLE 43

Temperature Coefficients of Adsorption for Various Gases

Gas.	ζ	ξ	Observer.
N_2	0·01780	0·005411	Homfray
N_2	0·01367	0·002970	Titoff
Ar	0·01387	0·002820	Homfray
CH_4	0·01517	0·004228	,,
C_2H_4	0·01117	0·003640	,,
CO	0·01515	0·003607	,,
CO_2	0·01420	0·003525	,,
CO_2	0·01420	0·004770	Titoff
NH_3	0·02168	0·009870	,,

What differs from gas to gas is, in the case of the isobars, a_0, that is, the amount adsorbed at 0° at different pressures—the adsorption isothermal of 0°. Each gas is characterized by the value of a_0 and of $\left(\frac{1}{n}\right)_0$. The values deduced from Miss Homfray's measurements are given in Table 44. It shows that in general the values of $\frac{1}{n_0}$ sink with increase of *critical temperature*, while a_0 increases with them. But great deviations are unmistakable; argon is less adsorbed—a_0 is too small, $\left(\frac{1}{n}\right)_0$ too great—than corresponds to its critical temperature. The same is true for CO_2.

TABLE 44

Adsorption Constants and Critical Temperature

Gas.	a_0	$\left(\frac{1}{n}\right)_0$	θ in degrees.
N_2	0·256	0·8683	— 146
CO	0·559	0·7605	— 140
Ar	0·224	0·8811	— 122
CH_4	2·691	0·5619	— 81·8
C_2H_4	23·72	0·2293	+ 10
CO_2	8·254	0·5298	+ 31

Still more striking in this respect is the behaviour of the two inert gases of still lower atomic weights, *neon* and *helium*. Fig. 24 reproduces measurements of Claude[1] plotted on the same scale as previously employed (cf. p. 110); it shows that the inert gases are comparatively much less adsorbed than hydrogen—neon 30 to 40 times less, although it has a

[1] Compt. rend. **158**, 861 (1914).

higher critical temperature than hydrogen. From the log a, log p curves it further follows that the values of $\frac{1}{n}$ are likewise much higher than those for hydrogen at the same temperature.

Hence we obtain no general simplification when we compare the gases at reduced temperatures. The values of $\frac{1}{n}$ certainly approximate more closely for many gases; we get, for example, for a reduced temperature

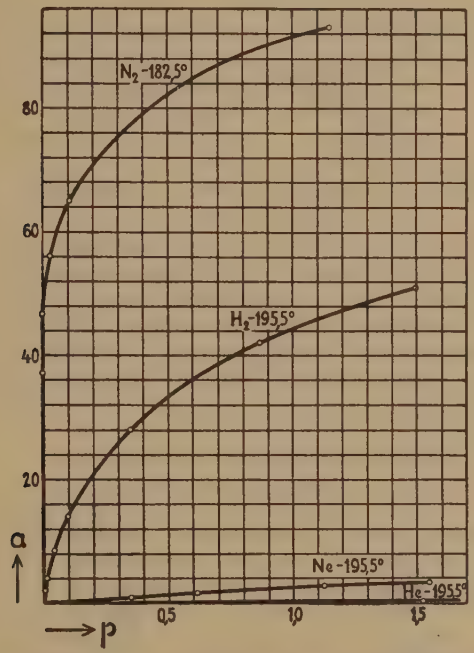


Fig. 24.—Adsorption Isothermals of various Gases, particularly inert Gases, on Charcoal.

of 1·2 the following table. But the anomalous behaviour of argon and carbon dioxide is again quite evident.

Table 45

The Adsorption Exponent $\frac{1}{n}$ at the Reduced Temperature 1·2

Gas.	Reduced Temperature 1·2 in degrees C.	$\frac{1}{n}$
N_2	— 121	0·2135
CO	— 113·4	0·3515
CH_4	— 43·6	0·3775
C_2H_4	+ 66·6	0·4717
Ar	— 91·8	0·6223
CO_2	+ 92	0·8541

For the same reason we cannot state definitely from what reduced temperature onwards $\frac{1}{n}$ takes the value 1. This is certainly, according to Miss Homfray's experiments, the case with

Argon	above	+ 48°
Nitrogen	,,	+ 100°
CH_4 and CO_2	,,	+ 182°

According to Titoff $\frac{1}{n}$ is 1 for,

Hydrogen	above	− 79°
Nitrogen	,,	+ 80°
CO_2	,,	+ 150°

In general it seems that $\frac{1}{n}$ may be put = 1 when the reduced temperature exceeds 2.

Evidently, therefore, two things have to be taken into account in the adsorption of gases by charcoal; firstly, the condensibility of the gases, that is, their behaviour as regards van der Waals' equation. This causes the slight specificity of the temperature coefficients ζ and ξ and the relation to the critical temperature. Along with this, specific peculiarities have a plain influence, such as the low adsorbability of the inert gases.

Gas-adsorption as a Consequence of Surface Attraction. Surface Layer several Molecules in Thickness

It is fruitful not merely to consider the adsorption of a gas from the point of view of the surface tension, but also to regard it directly as a surface attraction by the molecules of the adsorbent, as Eucken,[1] Polanyi,[2] Langmuir,[3] and A. M. Williams [4] have done. The arguments vary considerably, according as we assume the adsorption layer to consist of several layers of molecules or only of one. As I am at present unable to choose definitely between the two possibilities, they may both be dealt with at length: as an example of a theory postulating several layers of molecules, Polanyi's will be taken; and as an example of one depending upon only one layer, that of Langmuir.

As mentioned on p. 69, one can imagine the surface tension of a solid substance to be caused by the attractive forces which in a crystalline adsorbent, for example, holds the atoms together in the space-lattice; at the surface these forces are directed partly to the interior and partly to the exterior, and only the former are saturated. It is upon the saturation, by the gas molecules present in the external space, of this outward radiating part of the attractive forces (which are to be assumed both in the case of

[1] Ber. d. deutsch. physik. Ges. **16**, 345 (1914).

[2] Ber. d. deutsch. physik. Ges. **16**, 1012 (1914); **18**, 55 (1916); Zeitschr. f. Elektrochemie, **26**, 370 (1920); further *Berényi*, Zeitschr. f. physik. Chemie, **94**, 628 (1920).

[3] J. Amer. Chem. Soc. **38**, 2221 (1916); **40**, 1361 (1918).

[4] Proc. Roy. Soc. Edin. **38**, 23 (1918); **39**, 48 (1919); Proc. Roy. Soc. Lond. **96**, A, 287, 298 (1919).

crystalline and of amorphous solids), that the adsorption depends.[1] What the nature of this chemical binding is, remains an open question. I should prefer to regard it as even much looser than that which occurs in the case of molecular compounds ; as rather of the kind which occurs when the molecules of the same substance act upon one another, as is manifested, for instance, by the broadening of the spectral lines in a dense gas, or by the " molecular forces " in a liquid. According to the more recent theories of atomic structure, it would then be a question of the external quantum orbits of the electrons being greatly displaced, although not so far as in the case of an actual chemical compound. Since the latter is imagined as arising through the action of valency electrons, one might assume that the affinity of the atoms or molecules of a gas for electrons determines also the attraction between adsorbent and gas. In this respect we should have certainly to reckon with quite specific attractions. The extremely low adsorption of helium and neon would then agree with their

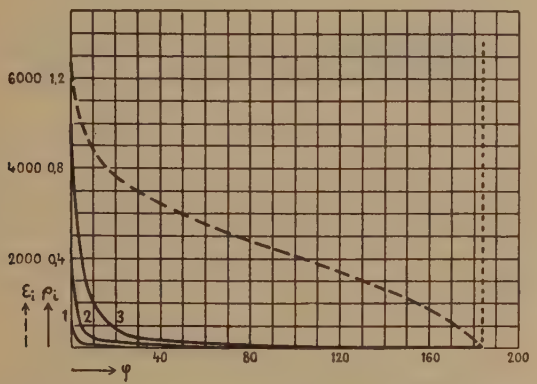


FIG. 25A.—ρ_i, φ and ε_i, φ Curves for CO_2 on Charcoal at 151·5°.

low affinity for electrons, which shows itself, for example, upon collision of these atoms with electrons of low ionization voltage.[2]

In any case, we may assume with Polanyi a gradient of potential directly at the surface of the adsorbent, and the *adsorption potential* ε_i at a distance i from the surface may be defined as the work gained when a molecule of the gas is brought from infinite distance to a distance i from the surface. Since in the external space no work is gained, the gain first commences at the limit of the adsorption layer, that is, at a distance δ from the surface. For the state of the gas in the adsorption space—the space, that is, enclosed between the surface of the adsorbent and the limit of the adsorption layer—we can distinguish three cases.

1. Above the critical temperature of the adsorbed substance no liquefaction occurs ; the gas is strongly compressed, and its density decreases with the

[1] See *Haber*, J. Soc. Chem. Ind. **33**, 50 (1914) ; Zeitschr. f. Electrochemie, **20**, 521 (1914) ; then also *Langmuir*, Met. Chem. Eng. **15**, 469 (1916) ; Phys. Rev. **6**, 79 (1915) ; **8**, 149 (1916) ; J. Amer. Chem. Soc. **38**, 2221 (1916) ; **39**, 1848 (1917) ; **40**, 1361 (1918) ; *E. Herzfeld* and *Klinger*, Beitr. z. physik. Chemie der Flüssigkeiten, Zürich (1919) ; *Schilow* and *Lepin*, Zeitschr. f. physik. Chemie, **94**, 25 (1920), and others.

[2] *J. Franck* and *Hertz*, Verh. d. deutsch. phys. Ges. **15**, 929 (1913).

distance from the surface in some such manner as is indicated by full-lined curves in Fig. 25 A and B (from Berényi). In these, the volumes φ of the adsorption space are plotted in cub. mm. per gram of charcoal, the distance from the zero representing not only the magnitude of φ, but also the distance from the surface of the adsorbent. This must be imagined as being to the

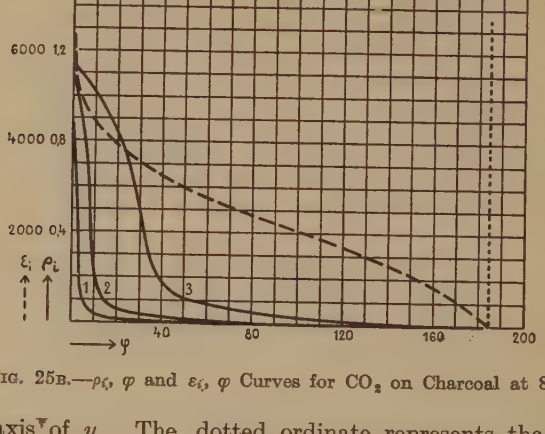


FIG. 25B.—ρ_i, φ and ε_i, φ Curves for CO_2 on Charcoal at 80°.

left of the axis of y. The dotted ordinate represents the limit of the adsorption space. The full curves have as ordinates the densities ϱ_i, that is, the amount adsorbed in a spatial layer divided by the volume of this layer. The figures refer to the adsorption of carbon dioxide by cocoanut charcoal, according to Titoff. In Fig. 25A (at 151·5°) we are therefore

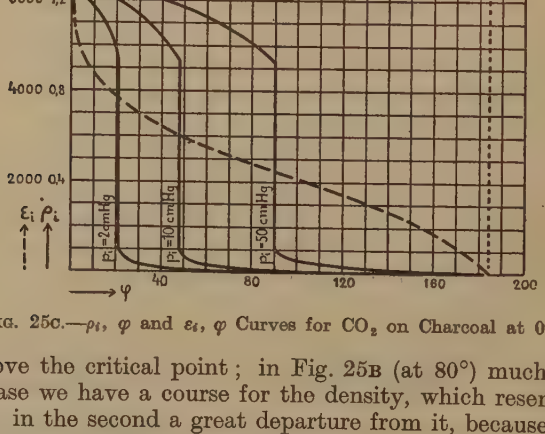


FIG. 25C.—ρ_i, φ and ε_i, φ Curves for CO_2 on Charcoal at 0°.

decidedly above the critical point; in Fig. 25B (at 80°) much closer to it. In the first case we have a course for the density, which resembles that of an ideal gas; in the second a great departure from it, because the van der Waals equation has to be taken into account.

2. Below the critical temperature (at 0°), but still far above absolute zero, the adsorption space immediately at the surface is filled (assuming complete wetting) with liquid, and its density changes very little, as shown in Fig. 25C, in accordance with the lower compressibility of the liquid.

The remainder of the adsorption space is filled with compressed gas, the density of which falls off in a similar manner to that represented in Fig. 25B.

3. At absolute zero the amount of matter which is present in the part of the adsorption space which is filled with gas may be regarded as so small that its density may be neglected as compared with that of the liquid; we may thus make the calculation as if only a part of the adsorption space were filled with liquid. The course of the curve will be quite similar at some distance above absolute zero, as is shown in Fig. 25D for a temperature of $-76{\cdot}5°$.

For case 3 the conditions are particularly simple. If for a pressure p_i on the adsorption isothermal, the amount of adsorbed liquid is a_i, it fills the

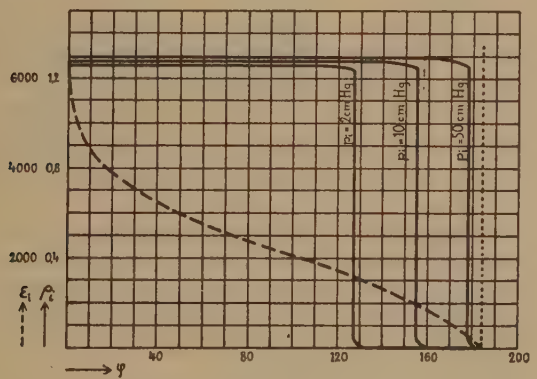


FIG. 25D.—p_i, φ and ε_i, φ Curves for CO_2 on Charcoal at $-76{\cdot}5°$.

adsorption space up to a distance i from the surface; for a second pressure p_i' the amount adsorbed is a'_i and the distance i'. The distance i of the limit of the liquid from the adsorbent is given by the fact that at that point the pressure in the adsorption space must be equal to that of the saturated vapour of the liquid. The quantities p and a of the adsorption isothermal are thus connected in a simple manner with the distance from the surface of the adsorbent.

The numerical connection is obtained by the following thermodynamical argument. If we neglect the differences between the internal pressure of the liquid in the adsorption space and that of the same liquid at the same temperature in the free space, then the work gained by bringing 1 mol. of the adsorbed substance from the external space into the adsorption layer is equal to the adsorption potential ε_i. The work gained by isothermal distillation must be equally great. Since the vapour pressure in the external space is p_i, corresponding to the pressure prevailing at adsorption equilibrium, and at the boundary i the pressure p_ϵ of the saturated vapour of the adsorbed substance condensed to a liquid, then this work is

$$\mathrm{RT} \log \frac{p_\epsilon}{p_i}$$

Therefore

$$\varepsilon_i = \mathrm{RT} \log \frac{p_\epsilon}{p_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If we neglect the variation in the density ϱ_f of the liquid with pressure, then

the volume φ_i in the adsorption layer which is filled with liquid—referred to 1 sq. cm. of the surface—is connected with the amount adsorbed a_i by the equation

$$\varphi_i = \frac{a_i}{\varrho_f} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we know p_i and a_i from a measured adsorption isothermal, if further p_ϵ and ϱ_f are known, we get from these two equations a relation between ε_i and φ_i, that is, the dependence of the adsorption potential upon the distance.

Polanyi calls this ε_i, φ_i curve the *characteristic curve* of adsorption, and therefore

$$\varepsilon_i = f(\varphi_i) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

as the *characteristic function* of adsorption. In Figs. 25 A to D it is represented by dotted curves, the ε_i values being given in gram-calories. The curve represents the dependence of the adsorption attraction upon the distance and ought—and this is the essence of Polanyi's view—to be independent of the temperature. If we have therefore obtained the characteristic function from an adsorption isothermal measured at one temperature, it may be used without any alteration for every other temperature.

It is only for the sake of lucidity that we have chosen above the argument as first developed by Polanyi, which only allows of the calculation of the characteristic adsorption function from an adsorption isothermal measured at very low temperature. Berényi has shown that we can also deduce the function from isothermals which lie above the critical temperature of the adsorbed substance.

If we have now found the characteristic adsorption function, the further process for calculating an adsorption isothermal at another temperature is as follows. We calculate ε_i as function of ϱ_i, the density of the adsorbed substance,

$$\varepsilon_i = g(\varrho_i) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

namely, for a given adsorption pressure p_i, a problem which corresponds to that formulated in equation (1); in this case we have only to add that in the former case equation (4) was simplified and calculated only for $\varrho_i = \varrho_f$, the density of the liquid, while this has now to be done for a more general range of values of ϱ_i. This calculation is quite independent of the nature of the adsorbent, and is a pure application of the equations of state of the gas and liquid.

By eliminating ε_i from equations (3) and (4) we get the density ϱ_i for the same p_i as a function of φ_i,

$$\varrho_i = h(\varphi_i) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

a calculation which corresponds to that carried out in equation (2). The full curves in Figs. 25 A to D are graphs of equation (5). From the density of the adsorbed substance in the adsorption space and the adsorption volume we get the amount adsorbed; since the density is in general variable, it is found by means of the equation

$$a = \int_{\varphi_i = 0}^{\varphi_\epsilon = 0} \varrho d\varphi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

We thus get the a belonging to a given p, and if the calculation is carried

out for various p values, we obtain the whole of the adsorption isothermals.

The calculation, by Polanyi and Berényi, of the results of Titoff, Miss Homfray, Patrick,[1] and Richardson,[2] gave throughout a satisfactory agreement with the theory, and in part a very good one, especially in the case of Titoff's measurements, which may be regarded as particularly trustworthy. How far the agreement goes here appears from Fig. 26, in which the points are the values found by Titoff for the adsorption of CO_2 on cocoanut charcoal; while the full curves are the theoretically calculated adsorption isothermals. From the isothermal for T = 273° the characteristic adsorption function was deduced. Departing from the usual practice, the adsorbed amounts are given in mg. per gram of adsorbent; the pressures, as usual, in centimetres of mercury. Figs. 25 A to D also refer to these experiments. Polanyi's theory therefore states quantitatively what was stated qualitatively on p. 121 above, namely, that we can deduce the whole sheaf of adsorption isothermals from a single one, and calculate them on the basis of the equation of state.

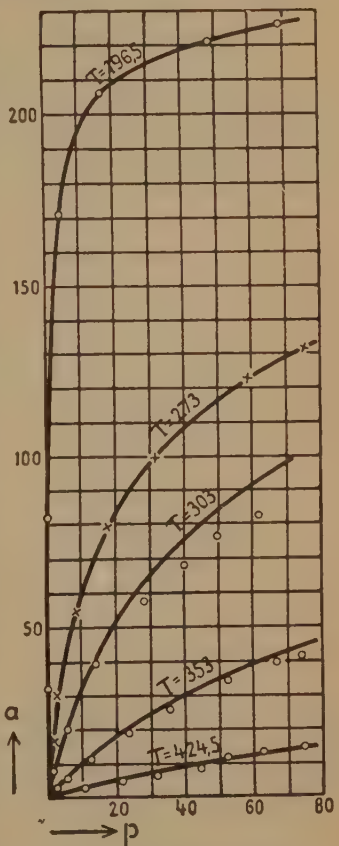


Fig. 26.—Adsorption Isothermals of CO_2 on Charcoal at various Temperatures.

This mode of considering the matter also allows deductions to be made concerning the form of the adsorption isothermals. At high temperatures and low pressures we may assume that Boyle's law is true in the whole adsorption space. Then, however, the amount adsorbed is simply proportional to the gas pressure, as Eucken pointed out; for if the molecules of the gas are independent of one another according to Boyle's law, then the attraction of the adsorbent will retain twice as much if twice as much is present in unit volume. The range of temperature discussed on p. 122, in which the adsorption exponent $\frac{1}{n} = 1$, in which therefore the adsorbed amount becomes proportional to the pressure, must be that range of temperature in which Boyle's law also holds for the adsorption space. This is true for lower temperatures as well, provided that the gas pressure is low enough.

If Boyle's law is not true in the adsorption space as well, then the adsorption isothermals must bend towards the p axis, the amounts adsorbed must increase less quickly than corresponds to proportionality. For the compressibility is smaller in condensed gases than is required by Boyle's law,

[1] "Die Aufnahme von Gasen durch das Gel der Kieselsäure." Diss., Gottingen, 1914: *McGavack* and *Patrick*, J. Amer. Chem. Soc. **42**, 946 (1920).

[2] J. Amer. Chem. Soc. **39**, 1828 (1917).

fewer molecules can be condensed in the adsorption space, and this is increasingly the case when below the critical point a portion of the quantity adsorbed is liquefied. The characteristic bending of the adsorption isothermals is thus produced. That the adsorption isothermals above the critical point differ so little from those below is comprehensible when we consider how similar the bending of the p, v curve of a gas, and therefore the behaviour of its compressibility immediately above the critical point, is to that of a p, v curve below the critical point.

It is, moreover, to be expected that the $\frac{a}{v^2}$ of van der Waals' equation will have, in the range in which gases depart from the ideal gas laws, a greater effect relatively to p than the b relatively to v; that is, the compressibility decreases at first less strongly with increase of pressure than in the case of an ideal gas. The amount adsorbed must therefore increase in this range faster with the pressure than in the initial range of small

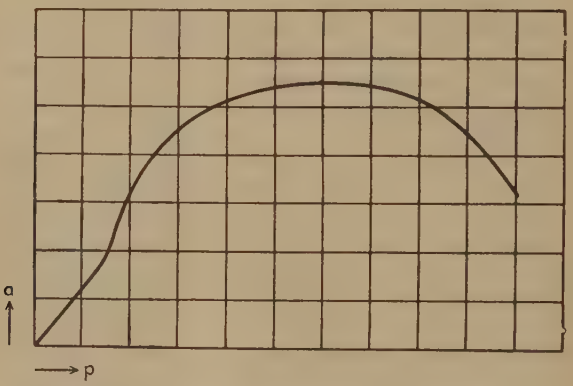


Fig. 27.—General Form of the Adsorption Isothermal of a Gas (very diagrammatic).

pressures, and only at still higher pressures does the a, p curve bend towards the p axis. We have, therefore, as Fig. 27 shows, a point of inflexion. Hitherto it has not been described. At quite high pressures the attraction of the surface does not have any effect, the amount adsorbed becomes zero, the a, p curve approaches the p axis, after it has passed through a range of *saturation*, that is, of a constant amount adsorbed (see Fig. 27). Saturation was closely approached, for example, by Titoff in the case of the adsorption of NH_3 by cocoanut charcoal at $-23{\cdot}5°$ and a pressure of one atmosphere. Fig. 27 therefore shows the general course which we might expect for the a, p curve at small pressures also.

The stoichiometric behaviour of the gas can also be defined more sharply according to Polanyi. He uses for comparison the adsorption potential ε_{max} for $\varphi = 0$—that is, in Figs. 25 A to D the values of the ordinates for zero value of the abscissæ—and finds that for many gases it is very nearly proportional to the square root of the van der Waals constant a_A (this constant is denoted here with a_A to distinguish it from the amount adsorbed a, hence

$$\varepsilon_{max} = k\sqrt{a_A} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The following table shows how far this equation is valid. The values of a_A are derived from an investigation of J. J. van Laar.[1] This relation is a confirmation of the theory supported earlier by Prince Galitzin [2] and D. Berthelot,[3] that the attraction between two bodies is proportional to the

TABLE 46

Relation between Adsorption Potential and van der Waals Constant a_A

Adsorbed Gas.	ε_{max} in g-calories.	$10^3 . \sqrt{a_A}$.	k
H_2	about 3,000	20·6	150
N_2	4,320	51·8	83
O_2	4,450	51·9	86
Ar	4,100	51·0	80
CH_4	5,230	60·8	86
C_2H_4	7,100	94·1	75
CO	4,840	53·0	91
CO_2	6,100	84·7	72

product of the square roots of a constant a_A. Since the one constant a_A, that for charcoal, does not change, equation (7) follows immediately from this. The above-mentioned relation of Galitzin and D. Berthelot does not appear to be generally valid, so that we are here dealing apparently only with a favourable limiting case.

The theory of Polanyi contains two assumptions which are surprising, in connexion with which it is necessary to test how far they agree with other experience. One is the independence on the temperature of the adsorption potential ε_i, and hence of the van der Waals constant a_A over so large a range of the temperature. This is, if we regard adsorption as fundamentally an electrical effect of the residual valencies, very curious, especially also from the standpoint of the electrical theory of the van der Waals attraction developed by Debye.[4] Debye shows how, merely upon the basis of the fact that we must ascribe to the molecules in gases or liquids movable, non-rigid electric charges, we arrive at an attraction due to the action of the molecular electric fields upon one another, which agrees as regards the order of magnitude with the van der Waals constant a_A; it is even possible by this means to calculate the order of magnitude of the surface tension of a liquid. According to this view, we should, however, expect a greater temperature coefficient than that assumed by Polanyi, especially for substances like SO_2, the molecules of which are pronounced dipoles. But precisely for the adsorption of SO_2 by silicic acid gels [5] the Polanyi theory is well borne out.

Secondly, the theory assumes that the adsorption layer consists of more than one layer of molecules. Many other experimental results, as we shall see later (cf. p. 315), tell in favour of this view, while theoretical grounds in particular make a single layer of molecules more probable as adsorption layer.

[1] Zeitschr. f. anorg. u. allg. Chemie, **104**, 66 (1918).
[2] Wied. Ann. **41**, 770 (1890).
[3] Compt. rend. **126**, 1856 (1898).
[4] Physik. Zeitschr. **21**, 178 (1920).
[5] *McGavack* and *Patrick*, *loc. cit.* p. 127.

The theory developed by A. M. Williams,[1] likewise on the assumption of an attraction between adsorbent and adsorbed body, appears to be less well founded than Polanyi's. Another expression for the adsorption isothermal which he obtains is noteworthy:

$$\log\frac{a}{p} = \mathrm{G} + \mathrm{H}a. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

G and H are constants; at lower pressures this expression agrees better than the usual adsorption isothermal.

Adsorption as Surface-attraction. Surface-layer only one Molecule in Thickness

Langmuir,[2] in contradistinction to Polanyi, does not assume any far-reaching forces, but allows the residual valencies projecting from the surface-layer to be saturated only by molecules which lie in a single layer. In the case of a crystalline adsorbent, a regular distribution, depending upon the space-lattice, of *points of residual valency*, will be present on the surface, at which points lie comparatively few saturated atoms or atomic groups of the adsorbent. If gas molecules impinge at these points, they adhere. If all the points of residual valency are occupied, further gas molecules upon impinging will be thrown back without adhering. He indeed discusses the possibility of layers which consist of two layers of molecules, but regards the case of the saturation of residual valency by a single layer of molecules as particularly frequent, and worthy of consideration.

He arrives at a formula for the adsorption isothermal in the following manner. For the velocity with which the molecules impinge upon the surface—considered for the present to be crystalline—we have by the kinetic theory[3]

$$\mathrm{m} = \sqrt{\frac{\mathrm{M}}{2\pi\mathrm{RT}}}p.$$

Here m is the weight in grams of gas which impinges in one second upon 1 sq. cm. of surface, p is the gas pressure, M the molecular weight. The number of molecules of gas which impinge upon 1 sq. cm. in a second is then

$$\mu = \frac{\mathrm{m}}{\mathrm{M}} = \frac{p}{\sqrt{2\pi\mathrm{MRT}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Let the fraction α of the impinging molecules remain adhering at any time, and let θ be that fraction of the surface, the residual valencies of which are regarded as *unoccupied*. The velocity of gas condensation upon a surface which is already partly occupied is then

$$\mu\alpha\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If the velocity of evaporation from a fully occupied surface is v, then that from a partially occupied one is

$$\mathrm{v}\theta_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

[1] *loc. cit.* p. 122.

[2] *loc. cit.* 122, particularly J. Amer. Chem. Soc. **40**, 1361 (1918). [For an account of Langmuir's theory of the atom and of valency, see *Loring*, "Atomic Theories."]

[3] *O. E. Meyer*, Kinetische Theorie der Gase, 1899, p. 82; *Langmuir*, Phys. Rev. **2**, 333 (1913).

where θ_1 is the *occupied* fraction of the surface. Naturally

$$\theta + \theta_1 = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In equilibrium (2) is equal to (3), hence

$$\theta_1 = \frac{a\mu}{v + a\mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Or if we put $\frac{a}{v} = \beta$

$$\theta_1 = \frac{\beta\mu}{1 + \beta\mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If now a is the number of mols. of gas adsorbed upon the square centimetre, then aN is equal to the number of adsorbed molecules, where N as always is the number of molecules per mol. This number aN must be equal to the number of residual valencies occupied in equilibrium. Let N_0 be the number of points of residual valency per square centimetre; then $N_0\theta_1$ is the number occupied in equilibrium, therefore

$$a = \frac{N_0}{N}\theta_1 = \frac{N_0}{N}\frac{\beta\mu}{1 + \beta\mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

a relation which represents the adsorption isothermal, since according to equation (1) μ is proportional to the pressure p. The adsorption isothermal has therefore for a crystalline adsorbent under the simplest conditions—that only one molecule of a gas occupies each point of residual valency—the form

$$a = \frac{\alpha'\beta'p}{1 + \alpha'\beta'p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where α' and β' are new constants.

Langmuir tested formula (8) by measuring the adsorption of various gases (methane and others) on mica at the temperature of liquid air and at very low pressures (between about 0·00015 and 0·01 cm. of mercury). The formula agrees well, in part better than the ordinary adsorption isothermal. The fact also agrees with his theory that the number N_0 of points of residual valency calculated from these experiments was smaller than the total number of atoms of the solid body per sq. cm. of surface.

In the case of an amorphous adsorbent, the points of residual valency are distributed irregularly upon the surface. A small portion of the surface $d\omega$ corresponds to the amount da adsorbed. Instead of equation (7) we get

$$da = \frac{N_0}{N}\frac{\beta\mu d\omega}{1 + \beta\mu}$$

and

$$a = \frac{N_0}{N}\int_0^1 \frac{\beta\mu d\omega}{1 + \beta\mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In the case of the adsorption of various gases upon glass—under similar conditions to those carried out with mica—a formula with three constants

$$a = \beta_1 + \frac{\alpha_2\beta_2 p}{1 + \alpha_2 p}$$

proved useful.

Langmuir's theory reckons with very diverse conditions. Points of residual valencies of different kinds, which are occupied by one or several molecules, may be present, and so on. We might ask the question how we are to explain according to the theory the fact that adsorption is fre-

quently so little specific, if the answer were not, that the number of thoroughly investigated adsorbents is not yet great.

The Influence of the Adsorbent upon Gas Adsorption

The adsorbents which have been examined hitherto are, almost without exception, solid foams. It is therefore, as already remarked, not at all the externally visible surface which comes mainly into question as the adsorption surface, but especially an *inner surface*, as to the extent of which our present appliances do not permit us to form any picture. Hence it is also not certain that powdering the adsorbent will increase the active surface. That would only be the case when dividing up the particles of an adsorbent having no inner surface. But if inner active surface already present is merely made into external surface, this does not alter the adsorption surface. Powdering may, however, adversely affect the adsorption if, for example, coarse pores are pressed together and access by diffusion to the inner surface is thus diminished. These considerations explain why the statements regarding the effect of powdering adsorbents, especially charcoal, in adsorption experiments are more or less contradictory. De Saussure [1] and Baerwald [2] mention a diminution in the amount adsorbed through powdering. The latter ascribes it in one case rightly to interference with diffusion. Chappuis [3] found in the case of cocoanut charcoal a slight increase, and Patrick [4] the same on powdering a silicic acid gel.

In comparing different adsorbents we must remember that the amount a adsorbed, which is referred to unit weight of adsorbent, does not permit of any proper comparison. It includes two quantities which must be separated: firstly, the *actual specific adsorptive power*, that is, the amount adsorbed per square centimetre of surface; and secondly, the *specific surface area* already mentioned, that is, the extent of the surface of 1 gram of adsorbent. Since we have at present no means of measuring the latter, every comparison between two adsorbents is in so far uncertain as we do not know whether they differ in specific adsorptive power—that is, in the expression $\frac{d\sigma}{dp}$ in the Gibbs equation—or in specific surface area.[5]

[1] *loc. cit.* p. 106.
[2] Ann. d. Physik (4), **23**, 84 (1907).
[3] *loc. cit.* p. 106.
[4] *loc. cit.* p. 127.

[5] *Paneth* [Z. für Elektrochemie, **28**, 113 (1922)] has recently shown that the specific surface of an adsorbent may be determined if a radio-active isotope of one of the atoms constituting it can be got. If finely powdered $PbSO_4$, for instance, be shaken with water containing RaD, the latter will be shared in the same proportion between the surface of the $PbSO_4$ and the liquid as are the lead atoms. Since we know the amount of lead in the saturated $PbSO_4$ solution, and can measure the partition of the RaD, the number of surface atoms of lead present can be deduced; it being assumed, of course, that the lead atoms in the interior of the crystals remain in their places. The method was tested by estimating the surface of the lead sulphate under the microscope, and gave a larger surface by about 30 per cent. This is quite to be expected, since the microscope must lead to a lower value for the surface owing to the finer irregularities in the crystal fractures being left out of account. Experiments on the adsorption of dyes upon the same sample of $PbSO_4$ lead to a result in favour of the single-molecule view of adsorption; at saturation the surface of the adsorbent was occupied only to the extent of about 31 per cent. See below, pp. 220, 314, and 818. This work also bears closely upon the question as to whether in the kinetic equilibrium between the vapour (or dissolved portion) of a solid and the crystal, the surface layer of molecules of the crystal alone are concerned, or whether deeper layers take part. The latter view is taken by *Bennewitz* [Ann. d. Phys. **59**, 193 (1919)], following *Planck's* sketch of a theory of vaporization in "Vorträge über die kinetische Theorie der Materie und der Elektrizität," Leipzig and Berlin, 1914, pp. 10 et seq. [Trans.]

It is therefore by no means necessary that every solid body, if sufficiently finely powdered, should adsorb strongly. The specific adsorptive power may be low in spite of the large surface.

A very general experience goes to show that a substance in the amorphous solid state adsorbs more strongly—the adsorptive power being referred to one gram of the adsorbent—than in the crystalline state. A good example of this is the adsorption of stibine (SbH_3) by antimony: the amorphous solid black antimony adsorbs the gas more strongly than when it has become crystalline.[1] It is highly probable that this phenomenon depends less upon a diminution in specific adsorptive power than upon a diminution of specific surface area. Even the smallest crystalline particles are coarser and more compact than the amorphous particles; they have a much smaller inner surface.

Since in the case of adsorption by the substance most investigated, namely carbon, the condensability of the gas usually has a far greater influence than the specific interaction between gas and adsorbent, it is not surprising that also in the case of adsorption by various adsorbents the peculiar properties of the adsorbent have little influence. It may be said with a certain degree of approximation that very frequently gases are adsorbed according to their condensability, and independently of the nature of the adsorbent; a relation

$$\left(\frac{a_1}{a_2}\right)_A = \left(\frac{a_1}{a_2}\right)_B = \left(\frac{a_1}{a_2}\right)_C \cdots$$

therefore holds, where A, B, and C denote various gases, and the adsorption values a are taken as measures of the adsorptive power of the adsorbents 1 and 2. Examples of this sort were given by de Saussure[2] for the adsorption of H_2, O_2, N_2, H_2S,NH_3 by charcoal, meerschaum, asbestos, hydrophane, different kinds of wood; and also by Hempel and Vater[3] for the adsorption of H_2 and N_2 on cocoanut charcoal, kieselguhr, pumice, platinum black; also in the case of adsorption by powdered glass, the gases arrange themselves in the order of their condensability.[4]

Naturally this rule, although frequently true, is not absolute. Departures must occur as soon as the specific action of the adsorbent becomes evident or the adsorption exponent $\frac{1}{n}$ is very different. For the adsorption potential ε_{max}, according to equation (7), p. 128, a rule of this kind must be more strictly true for the adsorption of different gases upon different adsorbents.

A good adsorption carbon such as cocoanut charcoal adsorbs hydrogen and nitrogen at $+20°$ about 3 to 8 times as strongly as kieselguhr, pumice, platinum black, and other adsorbents, and at the temperature of liquid air about 7 to 50 times as strongly.[5]

The conditions of importance for the preparation of a charcoal of maximum activity for gas adsorption are not yet accurately known. In any case, it is a question both of a large specific surface and of a large

[1] *A. Stock, Gomolka,* and *Heynemann,* Ber. d. deutsch. chem. Ges. **40,** 532 (1907). Also *Firth* [Zeitschr. f. physik. Chemie, **86,** 294 (1914)] remarks that cocoanut charcoal adsorbs more hydrogen the more amorphous it is.

[2] *loc. cit.* p. 106.

[3] Zeitschr. f. Elektrochemie, **18,** 724 (1912).

[4] *Mülfahrt,* Ann. d. Physik (4), **3,** 328 (1900).

[5] *Hempel* and *Vater, loc. cit.* under [3].

specific adsorptive power. A particularly large specific surface appears to be obtained when we strive to retain the structure as much as possible when carbonizing such organized structures as wood, fibres, blood, and the like: that is, we must ensure a very mild and cautious carbonization in order that particles originally separate may not unite, and so diminish the inner surface. The specific adsorptive power is no doubt lowered by difficultly volatile, tarry organic matters which result from carbonization, particularly humus bodies and the like, coating the inner surface; they diminish first of all the adsorptive power for other substances, since they are themselves adsorbed; and also shut off large parts of the inner surface from gas adsorption by closing pores leading to these parts. The heating of the wood must be conducted in such a manner, sometimes with addition of other suitable substances, that these difficultly volatile substances are removed as far as possible, either by their complete volatilization or by their carbonization. The Aussig method,[1] which was used during the war for preparing the charcoal employed for the breathing-filters of gas-masks, and consists in carefully heating the wood with zinc chloride solution, appears to combine both advantages, namely, a well-preserved surface, which is accessible through comparatively coarse pores, and an extensive destruction of all resinous bodies. A similar effect is obtained by treating wood or ordinary wood-charcoal with chlorine,[2] superheated steam, and other reagents. It is also possible to enhance the adsorptive power by dissolving out the injurious matters with organic solvents. A good and quick-acting adsorption charcoal must therefore be as far as possible free from tar. When this is the case, it is easily and quickly wetted by water, while feebly adsorbent, tarry charcoals are less easily wetted. This can be easily followed under a microscope; a small piece of a tarry charcoal prepared without particular care lies unwetted upon a drop of water, while a piece prepared according to the Aussig method is immediately wetted. The air contained in it escapes quickly in large bubbles; a fragment of cocoanut charcoal is also easily wetted, but its pores are so much finer that the air only escapes completely in fine bubbles after many minutes. Generally a baking temperature of 600° appears to be favourable.[3] However necessary a short heating at higher temperatures may sometimes be, it is apparently disadvantageous if long continued; the charcoal sinters too much and becomes crystalline.[4]

The Heat of Adsorption

Since adsorption decreases with rising temperature, we must expect, according to the principle of van 't Hoff and Le Chatelier, that it should take place with development of heat. This is actually the case. De Saussure already observed a rise of temperature during adsorption, as did later E. Mitscherlich,[5] Favre,[6] Chappuis,[7] Bitter [8] and others. Be-

[1] D.R.P. 290,656 of April 25, 1914.

[2] See also *Piutti* and *Mogli*, Gazz. Chim. ital. **40**, I, 569 (1910).

[3] *Hempel* and *Vater*, *loc. cit.* p. 133. They found that an animal charcoal which had been mixed with diluted ox-blood and reheated to 600° was considerably superior to cocoanut charcoal as regards adsorptive power.

[4] This was already known to *Th. Graham* [Pogg. Ann. **19**, 139 (1830)].

[5] Ann. de chim. et de phys. (3), **7**, 18 (1843).

[6] *Ibid.* (5), **1**, 209 (1874).

[7] Wied. Ann. **19**, 21 (1883).

[8] "Über die Erwärmung der Textilfasern in Gasen.," Diss., Würzburg, 1906. (The generation of heat by textile fibres in gases.)

sides charcoal, the substances used as adsorbents were meerschaum, asbestos (Chappuis), and fibres (Bitter). Quantitative experiments were made by Favre, Chappuis, Dewar,[1] and especially Titoff[2] and A. D. Lamb and Coolidge.[3] The majority of these measurements relate to the *integral heat of adsorption*, that is, the initial conditions are not quite definitely fixed—charcoal as gas free as possible and pure gas—and adsorption is continued until atmospheric pressure is reached. This heat of adsorption is similar to the heat of solution.

The *differential heat of adsorption*, which corresponds to a heat of dilution, is better defined; it is the amount of heat which is developed upon transition from one state of equilibrium between adsorbent and gas to another (with different gas pressure and different amount adsorbed).

It is useful to distinguish the following two cases. In the first case the amount adsorbed is practically constant at the different pressures and temperatures; all that changes is the gas pressure in equilibrium with this constant adsorbed amount. This *isosteric* heat of adsorption corresponds to the heat of evaporation; the one phase has an invariable composition, in the other the pressure changes. We are concerned with it in the range of intermediate and high pressures, in which the amount adsorbed changes but little, and the pressure comparatively greatly.

In the second case the pressure is constant while a and the temperature vary; the adsorbed amount changes with the temperature at a given pressure. This *isobaric* heat of adsorption is similar to a heat of reaction in a condensed system; the composition of one phase changes, while the pressure remains practically constant in the other. It concerns us most in the region of small pressures. In that region, as we recognize from the adsorption isothermal, the amount adsorbed may increase so strongly that the pressure compared with it may be regarded as constant.

For the isosteric heat of adsorption the same considerations apply as are used in deducing the equation of Clapeyron and Clausius; it may be calculated from the temperature coefficients ζ and ξ of the adsorption. Let there be a quantity of gas, adsorbed by an adsorbent, and so large that, upon the adsorption of further gas, a may be taken as unaltered; with this a a pressure p is in equilibrium. At a temperature higher by $d\mathrm{T}$ we have the same a, but a pressure greater by dp. For the isosteric heat of adsorption q_a of 1 c.cm. of gas at atmospheric pressure we have exactly as in the case of evaporation

$$-q_a = \frac{\mathrm{RT}^2}{22{,}410}\frac{d\log p}{d\mathrm{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

According to equation (10) on p. 119 we have for $\frac{d\log p}{d\mathrm{T}}$

$$\frac{d\log p}{d\mathrm{T}} = \frac{n}{\log_{10} e}(\zeta - \xi \log_{10} p),$$

the formula which holds for constant a and variable p, therefore for the conditions prevailing here. If we substitute this expression in the equation, we get

$$-q_a = \frac{n\mathrm{RT}^2}{22{,}410 \log_{10} e}(\zeta - \xi \log_{10} p). \quad . \quad . \quad . \quad . \quad (2)$$

[1] *loc. cit.* p. 107.

[2] J. Amer. Chem. Soc. **42**, 1146 (1920) ("Integral Heat of Adsorption of the Vapours of various Organic Substances on Charcoal").

[3] *loc. cit.* p. 107.

This equation was tested by Titoff. He determined ζ and ξ by measurements of the adsorption isothermals at different temperatures, and also measured, using the same adsorbent (cocoanut charcoal) and the same gases, the heat of adsorption by means of the ice-calorimeter; he was not satisfied with the integral heat of adsorption, but determined the differential heat by starting from, and ending with, known pressures. Table 47 shows that the equation (2) is satisfactorily confirmed.[1]

TABLE 47

Calculation of the Heat of Adsorption from the Temperature Coefficients of Adsorption. $t = 0°$

Gas.	ζ.	ξ.	q_a (calc.)	q_a (obs.)
Nitrogen	0·01367	0·00297	0·173	0·203
Carbon dioxide . .	0·01420	0·00477	0·2894	0·2908
Ammonia	0·02168	0·00987	0·3466	0·3539

Equation (2) allows of still further conclusions. On the one hand it follows that the heat of adsorption is particularly large at low pressures, hence for the first amounts adsorbed, and that it decreases with increasing pressure; since for low pressures log p has large negative values, and therefore $(\zeta - \xi \log p)$ large positive values. How plainly q_a decreases at still comparatively high pressures with increase of pressure appears from the following measurements of Chappuis [2]:

TABLE 48

Dependence of the Heat of Adsorption upon Equilibrium Pressure Adsorption of NH_3 on Meerschaum. $t = 0°$

p		a		q_a
Before.	After.	Before.	After.	
0	0	0	24·2	0·9164
0	0·5	24·2	48·3	0·5677
0·5	3·71	48·3	72·3	0·5074
2·93	21·50	72·3	95·3	0·4007
21·50	57·56	95·3	117	0·3402

Since, further, according to Table 43, ζ and ξ are not so very different from gas to gas, we obtain almost the same heat of adsorption for different gases, if we compare them in the same range of pressure and at temperatures at which they have approximately the same $\frac{1}{n}$. The values approximate at corresponding temperatures. If, on the contrary, we compare the gases at a given

[1] *Titoff* did not take those ζ and ξ values for calculation, which are deduced from the total course of an adsorption isothermal, but those which belong to the true range of pressure, that is, the range of pressure for which the heat of adsorption was measured.

[2] Wied. Ann. **19**, 29 (1883).

temperature, say 0°, we get a smaller heat of adsorption for the feebly adsorbed gases, for which $\frac{1}{n}$ is large, and larger heats of adsorption for the strongly adsorbed gases, for which $\frac{1}{n}$ is small. Table 47 shows this; from Tables 36 and 44 we can estimate the probable values of $\frac{1}{n}$. At temperatures above the critical point of the gases in question $\frac{1}{n} = 1$ and $\xi = 0$. The heat of adsorption approaches a constant limiting value

$$q_a = \frac{RT^2\zeta}{22{,}410 \log_{10} e}.$$

Equation (2) is only valid in the region of pressure and temperature, in which the $\log a$, $\log p$ straight lines spread out fan-wise. If this course were true for higher pressures as well, the straight lines would have to cut one another, $\xi \log p$ would be greater than ζ, the heat of adsorption would become negative. This does not appear, in general, to be the case. The $\log a$, $\log p$ lines, on the contrary, bend round, and approach a saturation; $\frac{1}{n}$ becomes almost zero, ζ and ξ are small. Equation (2) cannot then be any longer applied. Measurements by Hunter [1] and E. W. R. Pfeiffer [2] lead to this conclusion; they followed the adsorption of various gases up to high pressures (8 atmospheres) and at different temperatures.

For the total heat of adsorption we get the equation

$$dq = \left(\frac{\delta q_a}{\delta p}\right) dp + \left(\frac{\delta q_p}{\delta a}\right) da,$$

in which the first term on the right-hand side refers to the isosteric, and the second to the isobaric heat of adsorption.

According to the theory of Polanyi,[3] the total heat of adsorption may be connected with the adsorption potential. In the condensed range (Case 3, Fig. 25*d*) the total heat of adsorption q_M (calculated pro mol) is a sum of the following terms: the molar heat of compression w_M of the gas for compression from the equilibrium pressure p_i up to the saturation pressure p_s; the molar latent heat of evaporation λ_M; and the adsorption potential ε_i, which, of course, is the work required to bring a mol of the liquid from the external space into the adsorption layer; hence

$$q_M = \varepsilon_i + \lambda_M + w_M.$$

This equation agrees sufficiently well with measurements of Titoff on carbon dioxide. We see from this formula why the heat of adsorption is greater than the latent heat of evaporation of the liquefied gas.

Adsorption in Mixtures of Several Gases

Comprehensive investigations on adsorption in mixtures of several gases are not available. From the few results given by Joulin,[4] Miss Homfray,[5] Bergter,[6] Hempel and Vater [7] we can, however, form a sufficiently clear picture of the relations in question.

[1] Journ. Chem. Soc. **5**, 160 (1867); **6**, 186 (1868); **8**, 73 (1870); **9**, 769 (1871); **10**, 649 (1872).
[2] Beibl. d. Ann. d. Physik 1884, p. 630.
[3] *loc. cit.* p. 122. [4] *loc. cit.* p. 106. [5] *loc. cit.* p. 107.
[6] *loc. cit.* p. 108. [7] *loc. cit.* p. 133.

Of two gases in a mixture both are adsorbed; the one which is more strongly adsorbed in the pure state is also considerably more strongly adsorbed from a mixture, but both are adsorbed less strongly than if they were present in a pure state at the same partial pressure. The displacement from a surface of one gas by another thus takes place. The same equilibrium is reached whether we allow adsorption to take place from the mixture or add the second gas after adsorption of the first has taken place. The speed with which equilibrium is reached is in general smaller than in the case of the adsorption of pure gases, but appears to be greater in the case of direct adsorption from a mixture than when an adsorbed gas is subsequently displaced by a second. That adsorption from a mixture takes place more slowly is comprehensible when we consider that in the case of a pure gas the molecules at the beginning penetrate from outside into a space to a great extent gas-free; in the case of a mixture, on the other hand, the molecules of the one gas always diffuse into a space which contains molecules of the other, provided that both gases are not very strongly adsorbed. The adsorption equilibrium is quickly reached—in seconds or minutes—when a strongly adsorbable gas, such as chlorine or ammonia, is mixed with a slightly adsorbable one, such as air. Displacement should proceed more slowly for the reason that the surface and the pores of the adsorbent may sometimes be covered with a liquefied layer of the first gas, through which the second must diffuse in order to reach the surface.[1] We can take into account to a great extent the adsorption isothermals, especially when the gas with which we are dealing is present in small quantity and is strongly adsorbable.

The adsorption of the emanations of radium and thorium from mixtures with air or nitrogen by cocoanut charcoal[2] is to be regarded as an example of adsorption in a mixture of gases, and proceeds, as we should expect, according to the laws of adsorption. It agrees with the theory that at the excessively small concentrations of these radio-active gases the distribution follows Henry's law (see p. 127).

Drucker[3] has pointed out that the internal friction or viscosity in a mixture of gases is closely connected with the adsorption of the gases. The frictional surface formed between the moving gas and the layer remaining motionless upon the wall, certainly falls within the adsorption layer. Now, in the case of a mixture of two gases, the one more strongly adsorbed will have the most important share in the adsorption layer, even when the one more weakly adsorbed is in considerable excess in the mixture. We might therefore expect that the internal friction in the mixture as well would at first be only slightly different from that of the pure, more strongly adsorbed gas, and that only when the more weakly adsorbed gas begins greatly to exceed the other, would the viscosity approach the value that the more weakly adsorbed gas has in the pure state. Hence a great departure from the rule of mixtures occurs; the curve of the viscosity η as depending upon the partial pressure p of one of the gases is in general not a straight line joining the η values of the pure gases, but a curve strongly

[1] The inhibition is perhaps particularly strong, when the one gas is a saturated or almost saturated vapour; thus according to *Mülfahrt* (*loc. cit.* p. 133) the adsorption of CO_2 by glass-powder is greatly retarded in speed by moisture.

[2] See among others *R. W. Boyle*, J. Phys. Chem. **12**, 484 (1908); Phil. Mag. (6), **17**, 374 (1909); Le Radium, **7**, 200 (1910); *Satterly*, Phil. Mag. (6), **20**, 778 (1910); *v. Hevesy*, Physik. Zeitschr. **12**, 1222 (1911); *Mohr*, Ann. d. Physik (4), **51**, 549 (1916).

[3] Zeitsch. f. physik. Chemie, **92**, 289 (1918).

concave to the p axis. This is indeed the case with two inert gases such as a mixture of argon and helium, because argon is much more strongly adsorbed than helium (see p. 121). In the case of a mixture of oxygen and nitrogen, on the other hand, which are probably only slightly differently adsorbed at higher pressures, the η, p curve is almost a straight line; the rule of mixtures therefore holds, because the adsorption layer is not greatly different in its composition from the free gas.

On the adsorption of a gas by more than one adsorbent no results are available. If the adsorbents do not act upon one another, we should expect an equilibrium to be set up, in which the amounts adsorbed by the adsorbents are simply in equilibrium at the same pressure. The competition of two adsorbents for one adsorbed substance determines, according to Valentiner,[1] the phenomenon first described by Tammann,[2] in which a hot powder, such for instance as freshly heated charcoal-powder, adheres to a cold glass wall. The powder, gas-free on account of the heating, strives to remove adsorbed gas from the cold wall, and is held fast to the wall with the gas.

Adsorption and Chemical Processes

The influence of adsorption upon chemical processes may manifest itself either directly or indirectly: *directly*, by the displacement of a chemical equilibrium on account of adsorption; cases of this sort are not yet known with certainty. *Indirectly*, however, adsorption plays an important part in the chemical kinetics of gas reactions. For the decisive influence of the walls of the vessel in the case of these reactions should probably be almost entirely ascribed to the influence upon the velocity of the reaction exerted by the adsorption of the initial substances or of the end-products.

The direct displacement of equilibrium by adsorption cannot yet be dealt with in detail; we have not even fairly accurate theoretical and experimental data on adsorption in a mixture of several gases (see p. 138), and these form the basis for the treatment of this question. It is not, however, difficult to predict the direction in which the displacement will take place. Just as the adsorption of a pure substance proceeds in such a direction as to make the free surface energy a minimum, so should we expect that *the displacement of the chemical equilibrium will take place in the direction of favouring the formation of those substances which lower the surface tension with increase of pressure. The production of strongly adsorbable substances will therefore be favoured.*

Much more varied and better known are the indirect influences of adsorption upon the time-course of chemical reactions.

Here also two chief cases have to be distinguished; in the first, adsorbed substances react upon the surface of the adsorbent. The time-course of a true chemical reaction which is not inhibited by diffusion through the adsorption layer is measured. We have a *non-inhibited adsorption catalysis.* In the second, the time-course which is measured is not that of a chemical reaction, but of a diffusion process, and this proceeds in an adsorption layer. In this case adsorbed substances inhibit the process by influencing the diffusion. We have an *inhibited adsorption catalysis.*

[1] *Elster-Geitel*-Festschrift, p. 284 (1915).
[2] Ann. d. Phys. (4), **18**, 856 (1905); see also *W. Biltz, ibid.* **31**, 1050 (1910).

Non-inhibited Adsorption Catalysis

We have a particularly simple case of adsorption catalysis when only *one* initial material is present, which is adsorbed the most strongly of all the substances appearing in the reaction. Adsorption causes an acceleration of the reaction. It has hitherto been assumed that the strongly increased concentration in the adsorption space suffices to explain this accelerated reaction of the adsorbed substance, either because, being in itself labile, it decomposes more quickly in increased concentration, or because, for the same reason, it rapidly forms with the adsorbent an intermediate compound which quickly decomposes. According to Polanyi,[1] this circumstance does not suffice as an explanation. Thus, he estimates for the catalysis of oxy-hydrogen mixture at 600° on porcelain walls, according to Bodenstein's experiments,[2] an acceleration of the reaction at the surface of about 10^8-fold compared with the reaction in the free gas space. From the adsorption potentials ε_{max} for hydrogen and oxygen (3,000 and 4,400 cal.; cf. Table 46) the calculation gives, on the other hand, a 5 to 10-fold relative condensation upon the adsorbent, and hence an acceleration of the reaction about $10^{2 \cdot 5}$-fold; much less, therefore, than that observed. Polanyi therefore interprets the influence of adsorption otherwise. According to the calculations of J. J. van Laar,[3] the van der Waals a_A-values for the single atoms are considerably larger than those of the compounds, the values $\sqrt{a_A}$ mostly five to ten times greater. If equation (7) on p. 128 were generally true, it would follow from it that the adsorption potential ε_{max} is proportionately greater; it would therefore be of an order of magnitude of 25,000 cal. and more. This would, however, have the following consequences. The negative heat of dissociation of the molecules (H_2, O_2, N_2, etc.), otherwise so great, would be much smaller in the adsorption space, because the higher adsorption potential of the atoms would imply a considerable gain of heat fully capable of competing with the heat of dissociation. The adsorption space is therefore a space of strongly increased dissociation. Since the new molecules formed there by the reaction escape comparatively easily from the adsorption space, thanks to their smaller adsorption potential, their formation in the adsorption space is strongly accelerated. The slight dissociation of the molecules is, of course, an important cause of their slow reaction.

As regards the kinetics of such non-inhibited adsorption catalyses, Bodenstein and A. Stock [4] have found in the decomposition of stibine (SbH_3) an example which belongs to this group. The finely-divided antimony which is produced acts catalytically upon the reaction, and hence the well-known S-shaped curve of auto-catalysis appears. They assume that this catalytic action of the antimony arises out of the fact that SbH_3 is adsorbed upon it, and that the reaction goes faster in the surface layer on account of the increased concentration. The experimental conditions can be much simplified by employing an excess of antimony from the first. The additional amount produced by the decomposition can then be neglected, and

[1] Zeitschr. f. Elektrochemie, **27**, 142 (1921).
[2] Zeitschr. f. physik. Chemie, **29**, 665 (1899).
[3] Zeitschr. f. anorg. u. allg. Chemie, **104**, 105, 126, 144 (1918).
[4] Ber. d. deutsch. chem. Ges, **40**, 570 (1907); further also *A. Stock* and *Guttmann*, *ibid.* **37**, 901 (1904); *A. Stock*, *Gomolka*, and *Heynemann*, *ibid.* **40**, 532 (1907).

the surface area remains constant. The amount x adsorbed is, according to the adsorption isothermal, given by

$$x = \alpha p^{\frac{1}{n}}.$$

Now, according to the assumptions made, only the adsorbed SbH_3 and not that present in the gas space, should decompose, and the decrease with time of this adsorbed amount, $-\frac{dx}{dt}$, must be proportional to the amount adsorbed at any time. Compared with this decomposition, the adsorption equilibrium should adjust itself quickly, so that the adsorption isothermal always remains valid. Since further the change with time of the pressure, $\frac{dp}{dt}$, as measured by the manometer, is proportional to the amount decomposed—when we apply a certain correction which is rendered necessary by the great departure from the gas laws exhibited by SbH_3 (cf. note [1], p. 142)—we have the equation

$$-\frac{dp}{dt} = k'x = k'\alpha p^{\frac{1}{n}} = kp^{\frac{1}{n}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Upon integrating

$$k = \frac{1}{\left(1-\frac{1}{n}\right)(t_2 - t_1)}\left[p_1^{1-\frac{1}{n}} - p_2^{1-\frac{1}{n}}\right]. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This equation is actually fulfilled. In Table 49 are to be found values of k which are calculated according to this formula. For $\frac{1}{n}$ a value of 0·6 was chosen, which may reasonably be ascribed to SbH_3 at 25° in accordance with its condensability. The experimental conditions were such that the size of the surface remained practically constant. It is in accordance with the generally observed rise of the adsorption exponent $\frac{1}{n}$ with temperature that, according to a further investigation of A. Stock, Echeandia, and Voigt,[1] the exponent $\frac{1}{n}$, which must be introduced into the formula, increases with rise of temperature. The temperature coefficient of the reaction between 15° and 35° is, according to A. Stock, Gomolka, and Heynemann,[2] equal to 2, which agrees with the supposition that we are dealing with the time-course of a chemical reaction.

The decomposition of arsine (AsH_3) and phosphine (PH_3) [3] should also proceed according to this fundamental type. This appears to be contradicted by the fact that these processes proceed as reactions of the first order. But these decomposition reactions have been investigated at high temperatures (300° add over) at which the adsorption exponent $\frac{1}{n}$ certainly

[1] Ber. d. deutsch. chem. Ges. **41**, 1309 (1908).
[2] Ber. d. deutsch. chem. Ges. **40**, 545 (1907).
[3] *van't Hoff*, Étud. d. dyn. chim. 1884, p. 83; *Cohen*, Zeitschr. f. physik. Chemie **20**, 303 (1896); **25**, 483 (1898); *A. Stock, Echeandia* and *Voigt*, Ber. d. deutsch chem. Ges., **41**, 1319 (1908) (AsH_3); *Kooij*, Zeitschr. f. physik. Chemie, **12**, 155 (1893) (PH_3).

TABLE 49

Decomposition of SbH_3 on Solid Antimony. $t = 25°$

t (in minutes).	p^1 (relative Values).	k	t (in minutes).	p^1 (relative Values).	k
0	1·000	—	14	0·359	0·064
1	0·940	0·062	15	0·327	0·057
2	0·884	0·059	16	0·295	0·064
3	0·830	0·060	17	0·266	0·062
4	0·779	0·058	18	0·238	0·064
5	0·731	0·057	19	0·212	0·064
6	0·683	0·059	20	0·189	0·060
7	0·637	0·059	21	0·166	0·065
8	0·592	0·060	22	0·144	0·067
9	0·549	0·061	23	0·123	0·069
10	0·509	0·058	24	0·108	0·056
11	0·467	0·065	25	0·093	0·059
12	0·428	0·062	26	0·080	0·057
13	0·392	0·062			

approaches 1 (cf. p. 122) [2]; the equation (1) just used for the decomposition of SbH_3 passes into the equation for a reaction of the first order when $\frac{1}{n} = 1$. In agreement with this is the fact that the solid reaction products produce acceleration, and that the feebly adsorbed gases H_2 and N_2 have no influence upon the decomposition of AsH_3.[3] In the case of phosphine, Trautz and Bhandarkar [4] were able to show that above 672° the reaction proceeds as a pure gas reaction with a temperature coefficient of 1·8, while at lower temperatures the temperature coefficient decreases quickly, and the wall-reaction preponderates more and more.

These reactions are of extraordinary simplicity, in so far as the reaction products produce very little disturbance; the increase of the adsorbing surface by the formation of solid Sb, As, or P can be neglected if the adsorption surface is large at the outset; and the hydrogen, as a feebly adsorbed gas, is of little influence.

Bodenstein and Fink [5] include in this group, probably correctly, the decomposition of hydrogen selenide upon a selenium surface.

A second case in which the adsorbed gas reacts with the adsorbent is very frequent. According to Bodenstein and Karo,[6] the action of oxygen upon liquid sulphur is an example of this sort. Strictly speaking, the process should have been dealt with in an earlier section, in which chemical reactions at the interface liquid—gas should have been discussed. But since the present case is the sole one of the kind which has been investigated in detail, it is better introduced here. The velocity of this reaction is proportional to

[1] The pressures are not those directly observed, but are corrected upon the basis, of *van der Waals'* equation for the molecular attraction [see *Stock* and *Guttmann*, Ber. d. deutsch. chem. Ges. **37**, 908 (1904)].

[2] The critical temperature of PH_3 is 53°.

[3] *Cohen*, Zeitschr. f. physik. Chemie, **25**, 483 (1898).

[4] Zeitschr. f. anorg. u. allg. Chemie, **106**, 95 (1919). As to the connexion between reaction at the wall and in the free gas space, see *Trautz*, *ibid.* **104**, 189 *et seq.* (1918).

[5] Zeitschr. f. physik. Chemie, **60**, 46 (1907).

[6] Zeitschr. f. physik. Chemie, **75**, 30 (1911).

the size of the sulphur surface and to the first power of the O_2 concentration. The temperature coefficient of the process is large (1·87 for 10° at 252°). This may be interpreted to mean that the adsorbed O_2 reacts with the sulphur at its surface; since the temperature is comparatively high, and the critical point of oxygen very low, the adsorption exponent has the value 1; that is, the amount adsorbed is proportional to the O_2 concentration.

The SO_2 formed does not influence the velocity of the process. Bodenstein and Karo wish to explain this on the grounds that substances not immediately concerned in the reaction are not able to influence a process taking place in the surface layer any more than in the gas space. This cannot be correct; for if a substance not concerned in the reaction is strongly adsorbed, it will necessarily displace a less strongly adsorbed substance which reacts at the surface, and so lower its concentration there. The following explanation is more probable. Sulphur has the highest critical temperature of the three substances in question, and, at the temperature of the experiment, a considerable vapour pressure. The surface layer will therefore consist also on the vapour side mainly of sulphur molecules.[1] As regards SO_2 it is, so to speak, only a dilute solution; a displacement of O_2 by SO_2 will hence only take place in small measure.

This view of the reaction corresponds, according to Bodenstein and Fink,[2] to the formation of hydrogen selenide at selenium surfaces.

The time-course of the interaction between carbon and the O_2 adsorbed upon it, a process which in many respects is remarkable and important, is probably similar. The most detailed data about it we owe to Ch. B. Baker,[3] but de Saussure,[4] and later many other observers, have observed that the taking up of O_2 by charcoal is not a simple adsorption. According to Baker carbon dioxide could be pumped off quantitatively from an animal charcoal which had adsorbed moist O_2 in the cold (− 15°) and had then been heated for seven days at 100°. But if the carbon and oxygen had been carefully dried, no gas at all was obtained under similar experimental conditions at 100°; after heating for many hours at 450°, however, CO in preponderating amount, together with a little CO_2, was given off. It would thus appear as if carbon and oxygen yield at first CO, which is then oxidized to CO_2 by oxygen with water as catalyst according to the well-known results of Dixon.[5] Since, according to Heinr. Wieland,[6] formic acid appears as an intermediate product in this catalysis by H_2O, we might also seek for it in the interaction of moist oxygen and charcoal.

For the theory of the spontaneous combustion of freshly made wood-charcoal,[7] and particularly for that of coal-dust explosions, the adsorption of oxygen by charcoal and the interaction between the two is certainly of importance. In these cases, according to L. Wöhler,[8] the presence of iron oxide plays a part; a coal containing iron oxide sometimes explodes at a low temperature upon adsorption of oxygen, while one free from iron oxide does not.

[1] This corresponds to a view first put forward by *Reichinstein* (cf. p. 145).
[2] *loc. cit.* p. 142.
[3] Journ. Chem. Soc. **51**, 249 (1887).
[4] *loc. cit.* p. 106; among newer papers see e.g. *Lowry* and *Hulett*, J. Amer. Chem. Soc. **42**, 1408 (1920).
[5] See Ber. d. deutsch. chem. Ges. **38**, 2426 (1905).
[6] See Ber. d. deutsch. chem. Ges. **45**, 679 (1912).
[7] See e.g. *Hargreaves*, Journ. Chem. Soc. **27**, 420 (1874).
[8] Zeitschr. f. angew. Chemie, **31**, 192 (1918).

The interaction between charcoal and oxygen has also not been taken sufficiently into account in various statements in the literature. Thus it appears questionable whether the results of Bergter [1] really depend upon differences in adsorbability, when he finds that at low pressures (0·05 to 0·5 centimetres of mercury) O_2 is adsorbed many times more strongly than N_2, while at higher pressures they are adsorbed fairly equally.[2] At high pressures, therefore, the adsorbed air would have the same composition in the external space as in the adsorption layer, while at lower pressures much more O_2 would be contained in the latter. The statement of Dewar,[3] that the air adsorbed at − 190° by charcoal contains 56 per cent. of oxygen, might be correct if the adsorbability of O_2 and N_2 were different, and if at this temperature the velocity of reaction between O_2 and charcoal were sufficiently diminished.

Processes, in which two adsorbed substances react at the surface of the adsorbent, are frequent and generally important. A well-defined case of this sort has not yet been followed kinetically, so that it is not possible to say how far the following examples really belong to this group, and how far the initial materials or end-products inhibit the process. The following cases may be mentioned :—

If H_2 is led over a charcoal containing adsorbed Cl_2, HCl is freely developed.[4]

Cl_2 adsorbed on moist charcoal is hydrolysed to HCl ; [5] the O_2 developed probably unites quickly with the C to CO_2, in view of what has been said.

Phosgene is also decomposed to HCl and CO_2 upon adsorption on charcoal in presence of water.

The formation of phosgene from CO and Cl_2 on passing the gases over charcoal [6] is a technical method for the preparation of this substance.

The formation of sulphuryl chloride from SO_2 and Cl_2 and its decomposition take place on charcoal.[7]

Sulphuretted hydrogen is oxidized by oxygen to sulphur and water when charcoal, etc., are employed as catalysts.

In this group of processes the velocity will certainly depend upon the concentration of the two adsorbed materials at the boundary surface. Now since one substance displaces the other, we have the important conclusion that the velocity, as it varies with the concentration (or amount adsorbed, as the case may be) of each of the substances, passes through a maximum. If substance B is at first present in excess at the surface—which depends not only on the pressure in the gas space, but also on the adsorbability—the velocity increases with increase in the amount of substance A adsorbed ; the displacement of B thus caused is so small that it may at first be neglected.

[1] *loc. cit.* p. 108.

[2] Also the curious statement of *Bergter*, that nitrogen was adsorbed more strongly when mixed with oxygen than alone, must under these circumstances be regarded with caution. Might not more strongly adsorbable oxides of nitrogen be formed on account of an adsorption reaction ?

[3] Proc. Roy. Soc. **74**, 126 (1904).

[4] At the same time much Cl_2 is displaced from the charcoal by the HCl formed ; this results in cooling, because the heat of displacement and evaporation of the Cl_2 overcomes the other adsorption- and reaction-heats [*M. Berthelot* and *Guntz*, Compt. rend. **99**, 7 (1884)].

[5] *Melsens*, Ann. de chim. et de phys. (5), **3**, 522 (1874).

[6] *Paternò*, Gazz. chim. ital. **5**, 233 (1875).

[7] *Trautz*, Zeitsch. f. Elektrochemie, **21**, 329 (1915).

But as soon as A assumes values at the surface, which cause a considerable displacement of B, the velocity must finally decrease, because B is present at the boundary surface in ever-decreasing amounts. At a definite ratio of A to B the velocity will be a maximum. A behaviour of this sort has been observed qualitatively in the hydrolysis of phosgene on moist charcoal: its velocity increases at first with increase of moisture in the charcoal, reaches a flat maximum when the water-content amounts to 15 to 30 per cent., and assumes small values with a water-content of over 35 per cent.

This important deduction from the displacement occurring in the adsorption of several substances was first made quite definitely by Reichinstein, in, however, the rigid unconditional form of a so-called "Principle of displacement."[1] He assumes that with a given size of surface the number of adsorbed molecules of all substances present, independently of their concentration in the external space, is constant; hence

$$x + y + z = \mathrm{h} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Here x, y, z are the amounts adsorbed, h a constant. He further assumes, as is probably quite correct, that the molecules of the adsorbent take part in the building-up of the adsorption layer; x must therefore refer to the amount of adsorbent adsorbed. This assumption is of especial importance when the adsorbent has a considerable vapour pressure. The first assumption (Equation (3)) will never be strictly true, if only for the reason that the compressibilities of the substances are different. But with a certain degree of approximation it should frequently apply, particularly when we are dealing with monomolecular adsorption layers. In the case of the adsorption of several substances, it does in fact appear (cf. p. 200) that in the case of two substances the total amount adsorbed is about the same as when the more strongly adsorbable body is adsorbed alone; in the cases in question we can, with some justification, regard the number of molecules of the solvent in the adsorption layer as equally great.

Reichinstein is perhaps right in explaining by means of this theory the phenomena in which the maximum of an effect appears as the concentration of the one adsorbed substance increases; thus, for example, the well-known maximum in the velocity of the oxidation of phosphorus by oxygen, and its consequent luminosity in an O_2 atmosphere. The reaction must be practically limited to the adsorption layer. Let the velocity of oxidation v be proportional (the surface area of the phosphorus being constant) to the adsorbed amounts x and y; here x is the amount of the phosphorus, y that of the oxygen in the adsorption layer. Hence

$$\mathrm{v} = kxy,$$

where k is a constant. Now according to equation (3)

$$x + y = \mathrm{h}$$

hence

$$\mathrm{v} = kx(\mathrm{h} - x)$$

an equation for the velocity of reaction, which gives a maximum for the velocity at

$$x = \frac{\mathrm{h}}{2}.$$

Among the gas-reactions which Reichinstein explains on the basis of

[1] "Die Eigenschaften des Adsorptionsvolumens." Zürich and Leipzig, Gebr. Leemann u. Co.: 1916, p. 40, *et seq.*

this theory, the following may be mentioned: the maximum, observed by Ewan,[1] of the velocity of oxidation of aldehyde by oxygen; a mixture of phosphine and oxygen explodes upon expansion,[2] as also a mixture of silicon hydride and oxygen[3]; in glass vessels, the ignition temperature of oxy-hydrogen mixture falls from 620° to 540° when the pressure is reduced from 76 to 36 cm. of mercury[4]; there are many others. In all these cases the wall of the vessel is to be regarded as the adsorbent. Since we are always dealing with two gases, of which one—oxygen, or, in the case of oxy-hydrogen mixture, hydrogen—has a considerably lower critical point than the other, a change in the pressure will cause a change in the ratio of the amounts adsorbed, and we may arrive at values of this ratio, for which the velocity of the reaction in the adsorption space is greater than with the higher pressures at first present.

Inhibited Adsorption Catalysis

The state of affairs in the case of inhibited adsorption catalysis is very complex and diverse. In many cases it is a question of the diffusion of one of the reacting gases through a layer resting upon the adsorbent. For processes of this kind the general principles developed by Nernst[5] and Brunner,[6] which had previously been applied by Stefan[7] and Noyes and Whitney[8] to the velocity of chemical reactions, hold. If a process consists of a number of successive stages, the velocity of the whole process depends on that of the slowest component stage. Since diffusion proceeds comparatively slowly, it is often possible that diffusion is the slowest process taking place, and therefore determines the speed of the whole. Thus, for example, according to Stefan, the evaporation of a liquid proceeds as follows: Immediately at the surface saturation with vapour takes place very quickly. If at a distance δ from the surface a lower vapour pressure is maintained artificially (say by a current of air blown over the surface), the velocity of evaporation depends only upon the speed with which the vapour diffuses through the surface layer δ. According to the theory of diffusion the velocity of evaporation v is proportional to the diffusion constant D, the size of the surface of the liquid ω, and the gradient of pressure $\frac{dp}{dx}$; for the latter we may employ the difference quotient $\frac{p_s - p}{\delta}$, where p_s is the pressure of the saturated vapour, and thus obtain

$$v = \frac{D\omega(p_s - p)}{\delta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In the case of inhibited adsorption catalysis the conditions are still more complicated, inasmuch as the diffusion layer is an adsorption layer, and the process may depend upon the diffusion of more than one gas. We will therefore deal in detail with the catalysis of the reaction

$$2SO_2 + O_2 = 2SO_3$$

[1] Zeitschr. f. physik. Chemie, **16,** 315 (1895).
[2] *van de Stadt,* Zeitschr. f. physik. Chemie, **12,** 322 (1893).
[3] *Friedel* and *Ladenburg,* Lieb. Ann. **143,** 118 (1867).
[4] *A. Mitscherlich,* Ber. d. deutsch. chem. Ges. **26,** 399 (1893).
[5] Zeitschr. f. physik. Chemie, **47,** 52 (1904).
[6] *Ibid.* **47,** 56 (1904).
[7] Sitzungsber. d. K. Akad. d. Wiss. Wien, **68,** II. 385 (1873); **98,** II. 1418 (1889); Wied. Ann. **41,** 723 (1890).
[8] Zeitschr. f. physik. Chemie, **23,** 689 (1897).

on a platinum surface, which was carefully investigated by Bodenstein and Fink.[1]

Of the three substances appearing in this equation, SO_3 has by far the highest critical temperature. It will therefore be the most strongly adsorbed at the high temperatures in question, and hence forms on the surface of the adsorbent an adsorption layer, which becomes steadily greater as the reaction proceeds; it contains more SO_3 and so is thicker and denser. If now SO_2 and O_2 combine at a sensible speed only at the surface of the platinum, then the SO_3 layer will have an inhibitory action, since the initial substances must diffuse through it. The observed velocity of the process is thus composed of the purely chemical velocity at the surface and the velocity of diffusion. The velocity of the chemical reaction is in this case very great; whether we are dealing with an adsorption reaction, or whether with the formation of an intermediate compound with the platinum, is still an open question, although the first assumption is the more probable (cf. p. 150). The slow process of diffusion therefore controls the rate, but, in contradistinction to the simple cases discussed by Nernst and Brunner [2] and others, the diffusion path is variable, on account of the adsorption.

Hence only the velocity of diffusion through the variable layer is measured. Both O_2 and SO_2 diffuse; since the former diffuses more quickly, it will also be present in excess at the surface of the adsorbent as long as it is supplied in an amount equivalent to, or in excess of, the SO_2. The diffusion of the SO_2 alone will therefore condition the velocity of the process. Therefore, according to the law of diffusion,

$$\frac{d(2SO_3)}{dt} = \varkappa \frac{D_{SO_2}}{\delta} \{L_{SO_2}(2SO_2)_g - (2SO_2)_w\} \quad . \quad . \quad . \quad . \quad (5)^3$$

Here the quantities in brackets always denote concentrations; $(2SO_2)_g$ is the concentration in the gas space, $(2SO_2)_w$ that at the surface; L_{SO_2} is the solubility of SO_2 in the layer. Hence

$$[L_{SO_2} \cdot (2SO_2)_g - (2SO_2)_w]$$

denotes the fall in concentration; D_{SO_2} is the coefficient of diffusion of SO_2, δ the variable thickness of the layer, and $\varkappa$ a constant.

The thickness δ increases with increasing concentration of SO_2 in the gas phase. It is possible, as has been said, that the layer may become both thicker and denser. But even in the latter case a diminution of the velocity of diffusion, probably proportional to the increasing density, will occur; it is therefore simpler and sufficient to assume an increase in thickness. The amount adsorbed is equal to the volume of the layer $\omega\delta$ multiplied by its density ϱ, and for this amount the adsorption isothermal holds; hence

$$\omega\delta\varrho = \alpha'(2SO_3)^{\frac{1}{n}},$$

consequently

$$\delta = \frac{\alpha'}{\omega\varrho}(2SO_3)^{\frac{1}{n}} = \alpha(2SO_3)^{\frac{1}{n}} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

[1] *loc. cit.* p. 142; further *Fink*, "Die Kinetik der Kontaktschwefelsäure." Diss.; Leipzig, 1907.

[2] *loc. cit.* p. 146.

[3] The rate of formation of the SO_3 has not been put equal to the velocity of diffusion, but only taken as proportional to it, since the diffusion takes place through a moving layer; for the SO_2 layer grows, on account of the reaction, from the surface into the gas space, in a direction opposite to the direction of diffusion.

If we substitute this in equation (5), further remember that, on account of the rapid reaction at the surface, $(2SO_2)_w = 0$, and unite the constants to a single one k_y, we get

$$\frac{d(2SO_3)}{dt} = k_y \frac{(2SO_2)_g}{(2SO_3)^{\frac{1}{n}}}$$

or, denoting the amount of SO_3 formed by x and the initial concentration of the $(2SO_2)$ by y,

$$\frac{dx}{dt} = k_y \frac{(y-x)}{x^{\frac{1}{n}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If we put for the adsorption exponent $\frac{1}{n}$ the value $\frac{1}{2}$,[1] then integration gives

$$k_y = \frac{1}{t}\left\{y^{\frac{1}{2}} \log \frac{y^{\frac{1}{2}} + x^{\frac{1}{2}}}{y^{\frac{1}{2}} - x^{\frac{1}{2}}} - 2x^{\frac{1}{2}}\right\} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The following table from Fink's experiments shows on the one hand that the formula is essentially valid, and further, that as we should expect an excess of oxygen does not influence the velocity of reaction. A platinum gauze with a surface of about 6,400 sq. cm. served as adsorbent

TABLE 50

Adsorption Catalysis of SO_3 Formation with O_2 in Excess. t = 248°

$2SO_2$ = 129·6 mm. Hg. O_2 = 129·6 „ „			$2SO_2$ = 123·0 mm. Hg. O_2 = 492·0 „ „		
t (in minutes).	x (mm. Hg).	k_y.	t.	x.	k_y.
5	31·2	0·212	5	29·5	0·204
10	48·1	0·223	10	44·9	0·212
15	58·6	0·217	15	56·5	0·218
20	68·4	0·221	20	65·6	0·221
25	76·1	0·222	25	73·5	0·226
30	82·4	0·223	30	79·6	0·238
35	87·2	0·219	35	85·9	0·236
40	91·4	0·216	40	90·7	0·238
50	99·2	0·217			
60	104·8	0·216		Mean	0·222
	Mean	0·219			

When SO_2 is in excess, it will diffuse to the surface more rapidly than oxygen on account of the steeper gradient. As long as the excess is only small, a store of oxygen will be present on the surface of the platinum on account of its greater diffusion constant. With a certain definite excess, both gases will reach the surface equally quickly. Here the velocity of reaction will be equal to the velocity of diffusion of the two gases. If the

[1] This is justified ; the temperature was generally 248° ; the critical temperature of SO_3 is 216° according to *Schenck* (Lieb. Ann. **316,** 1 (1901)]. According to *Titoff*, the adsorption exponent $\frac{1}{n}$ for CO_2, in a range of pressure such as we are dealing with here, and at the critical temperature 30°, has the value 0·55.

concentration of the SO_2 in the gas space increases still further, O_2 and SO_2 exchange parts; the latter is now in excess at the surface, and the velocity depends in exactly the same way upon the velocity of diffusion of the oxygen as it previously did upon the velocity of diffusion of the SO_2. The following equation therefore holds:

$$\frac{d(2SO_3)}{dt} = k_z \frac{(O_2)_0}{(2SO_3)^{\frac{1}{2}}}$$

or

$$\frac{dx}{dt} = k_z \frac{z - x}{x^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where z is the initial pressure of O_2. In actual fact the constants calculated from equation (8) do not hold for considerable excess of SO_2, but those calculated from the equation

$$k_z = \frac{1}{t}\left\{z^{\frac{1}{2}} \log \frac{z^{\frac{1}{2}} + x^{\frac{1}{2}}}{z^{\frac{1}{2}} - x^{\frac{1}{2}}} - 2x^{\frac{1}{2}}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

do hold, as given in Table 51.

TABLE 51

Adsorption Catalysis of the Formation of SO_3 with SO_2 in Excess. $t = 248°$

$2SO_2 = 219{\cdot}7$ mm. Hg.
$O_2 = 107{\cdot}8$ „ „

t (in minutes).	x (mm. Hg).	k_y.	k_z.
2	21·7	0·165	0·350
5	36·0	0·146	0·336
10	51·5	0·132	0·329
15	63·5	0·125	0·340
20	72·1	0·117	0·343
25	78·5	0·109	0·343
30	83·3	0·101	0·340
35	87·0	0·094	0·334
40	89·1	0·086	0·317
45	93·4	0·084	0·338
50	96·1	0·079	0·342

The above theory is even capable of predicting the ratio of the concentrations of SO_2 and O_2 at which formula (8) ceases to be valid and formula (10) must be applied. This is clearly the case when O_2 and SO_2 reach the surface equally quickly. But in this case

$$\frac{dx}{dt} = k_y \frac{y - x}{x^{\frac{1}{2}}} = k_z \frac{z - x}{x^{\frac{1}{2}}}$$

Hence must

$$\frac{y - x}{z - x} = \frac{k_z}{k_y}.$$

$\frac{k_z}{k_y}$ was given by several series of experiments as $= 1{\cdot}56$. In order to recognize at what ratio of concentration formula (8) ceases to be valid, a

series of experiments by Fink may be quoted, in which the SO_2 excess is at first small, and the ratio of the concentration moves over the critical range in the course of the experiments. The constants are calculated from minute to minute in order that changes may be more accurately perceived.

TABLE 52

Adsorption Catalysis of the Formation of SO_3 with Small Excess of SO_2
$t = 248°$

$2SO_2 = 328{\cdot}5$ mm. Hg.
$O_2 = 298{\cdot}7$,, ,,

t (in minutes).	x.	k_y.	$\frac{y-x}{z-x}$	k_z.
10	92·0	0·218	1·14	0·244
20	132·9	0·201	1·18	0·235
30	165·9	0·227	1·22	0·271
40	190·8	0·221	1·27	0·276
50	209·9	0·213	1·33	0·278
60	225·6	0·209	1·41	0·286
70	239·2	0·213*	1·50*	0·309
80	250·4	0·211*	1·62*	0·327
90	259·1	0·198	1·75	0·326
100	266·6	0·184	1·93	0·346
110	272·3	0·156	2·13	0·315

We see that, from the points marked * onwards, where the quotient $\frac{y-x}{z-x} = 1{\cdot}50$ and 1·62 respectively, a decided and continued decrease of the values of k_y actually takes place.

The influence of foreign gases and of the temperature coefficient (1·36 in the range 186° to 247°) also fit into this explanation. Bodenstein and Fink correctly emphasize, however, that the temperature coefficient of a reaction of the kind just described does not allow any conclusion to be drawn as to whether or no we are dealing with a diffusion process. For in equation (5), not only is the diffusion coefficient dependent upon the temperature, but also δ—since α' in equation (6) is sensitive to temperature—and L_{SO_2}. It is hence quite possible that a large temperature coefficient may be observed if one of these other quantities—L in particular—changes considerably with the temperature.

We may further inquire whether the action of the surface of the catalysts in this reaction is due to adsorption of the reacting substances O_2 and SO_2 or to the formation of intermediate compounds? In the first place, the experiments of Küster [1] and Berl,[2] which were carried out with the pentoxides of vanadium and arsenic respectively, may be calculated in exactly the same manner as the experiments with platinum. A detailed examination of the question was undertaken by L. and P. Wöhler and W. Plüddemann [3]; very diverse catalysts were included, both those in which an intermediate reaction is probable (Fe_2O_3, Cr_2O_3, etc.) and those where it is practically impossible (Al_2O_3, SiO_2, etc.). They all behaved

[1] Zeitschr. f. anorg. Chemie, **42**, 453 (1904).
[2] Zeitschr. f. anorg. Chemie, **44**, 267 (1905).
[3] Zeitschr. f. physik. Chemie, **62**, 641 (1908).

so similarly that one is inclined, with Bodenstein and Fink, to regard the rapid reaction of SO_2 and O_2 at the surface of the catalyst as an adsorption catalysis.

To this group of adsorption catalyses belongs, according to Bodenstein and Fink,[1] the catalysis of oxy-hydrogen mixture on platinum at intermediate and lower temperatures.[2] In this case, again, the velocity of reaction is proportional to the first power of the concentration of the gas present in excess; only here the thickness of the adsorbed layer is, on account of the experimental arrangement, constant during the course of the reaction.

We can further classify in this group, according to the same investigators, the decomposition of CO into CO_2 and C on nickel and cobalt surfaces,[3] and the formation of CO_2 from CO and O_2 in porcelain vessels.[4]

Particular relationships appear when quartz glass is the adsorbent, partly for the reason, apparently, that it is very porous; we cannot therefore any longer neglect the velocity of adsorption as high compared with the velocity of diffusion. It determines the velocity of reaction, either alone or in conjunction with the diffusion. Above all, the displacement of reacting substances by reaction products is now also slow, and causes disturbance by clogging. This was the experience of Bodenstein and Kranendieck [5] in the case of the decomposition of NH_3 and SO_3 on quartz glass.

In the case of the oxidation of CO by oxygen to CO_2 on quartz glass, Bodenstein and Ohlmer [6] described the curious fact that CO inhibits its own combustion. Such behaviour is possible if the CO forms an adsorption layer through which the oxygen must diffuse. But since, according to what has been said, quartz glass is not at all an ideal adsorbent, and since further CO_2, which we might also imagine plentiful in the adsorption layer, does not influence the process, this conclusion should only be drawn with caution.

It quite seems as if, in the case of reactions in which carbon monoxide is concerned, unusual conditions prevail. This is, for example, striking in the case of the decomposition of nickel carbonyl according to the equation

$$Ni(CO)_4 = Ni + 4CO,$$

a reaction the course of which upon nickel surfaces was investigated by Zisch.[7] We might at first expect a course as in the case of the decomposition of stibine (SbH_3) mentioned above, since we might ascribe to the $Ni(CO)_4$, on account of its much higher critical point, a much greater adsorption than to CO. This is not the case. On the contrary, the CO formed in the reaction has a strong inhibitory action, whereas when added beforehand it either has no effect or one much slighter. This inhibitory

[1] Zeitschr. f. physik. Chemie, **60,** 59 (1907).

[2] *Bodenstein*, Zeitschr. f. physik. Chemie, **46,** 725 (1903). The catalysis of oxy-hydrogen mixture depends in a curious and still unexplained manner upon the nature of the adsorbent; see also *Bodenstein* [Zeitschr. f. physik. Chemie, **29,** 665 (1899)]; *Bone* and *Wheeler* [Phil. Trans. **206,** 1 (1906)]; *Rowe* [Zeitschr. f. physik. Chemie, **59,** 41 (1907)]; *J. R. Thompson* [Phys. Zeitschr. **14,** 11 (1913)] and others.

[3] *Schenck* and *Zimmermann*, Ber. d. deutsch. chem. Ges. **36,** 1231 (1903); *Smits* and *L. K. Wolff*, Zeitschr. f. physik. Chemie, **45,** 199 (1903).

[4] *Kühl*, Zeitschr. f. physik. Chemie, **44,** 385 (1903).

[5] *Nernst*-Festschrift, p. 99 (1912) (Decomposition of NH_3 on quartz glass); Zeitschr. f. physik. Chemie, **80,** 148 (1912) (Decomposition of SO_3 on quartz glass).

[6] Zeitschr. f. physik. Chemie, **53,** 166 (1905).

[7] According to experiments not yet published. It would further be worthy of investigation, how far metals have a particular power of adsorption for their own gaseous compounds (nickel for nickel carbonyl, antimony for antimony hydride, etc.); according to *Stoffel* [cited from Kolloidzeitschr. **12,** 59 (1913)], iron penta-carbonyl is also adsorbed by iron according to the usual adsorption isothermal.

action appears, indeed, even before the counter-reaction, formation of $Ni(CO)_4$ from Ni and CO, has proceeded far enough to be taken into account. The CO formed in the reaction "adheres," as it were, to the surface and blocks the admission of the $Ni(CO)_4$. Empirical formulæ may be found which reproduce this inhibited course of the reaction; but they are still without physical meaning for us.

Quite generally we may say of gas-reactions influenced by solid substances that if the velocity of the process is only dependent upon a single initial substance—usually proportional to its first power—or if it is inversely proportional to the first or a fractional power of one of the initial substances or end-products, then the velocity of the process will in all probability be conditioned by diffusion through an adsorption layer. But it must certainly be noted that inhibition alone, as evidenced by the process being inversely proportional to the concentration of a reacting substance, does not necessarily depend upon the action of a diffusion layer. We shall often have to remember that displacement, as preferred by Reichinstein (p. 145), can also exert a similar influence.

Particular Cases of Adsorption and Sorption

In the case of every solid surface in contact with a gas the adsorbed layer of gas must be taken into account. Here we are not referring to the thin layers of water which cover wettable surfaces, and which will be discussed later (p. 167) in dealing with adsorption in the neighbourhood of saturation pressure. Thus, according to Gaede,[1] even in the case of hydrogen on glass at pressures above 0·0001 cm. and at room temperature, a "skin" of gas, i.e. an adsorbed gas-layer, made its influence felt during the investigation of the external friction of this gas.

Also, the last residues of gas which have to be removed in the production of high vacua, are the quantities of gas present in the adsorption layer. The difficulty in removing them does not depend merely upon the fact that they have sometimes to diffuse out of fine pores, but also, in part, simply upon the characteristic shape of the adsorption isothermal.

This is also the cause of the firm adherence of odoriferous substances of high molecular weight to walls, textiles, hair, and the like[2]; this adherence is further accentuated since with the high critical points of these substances the adsorption exponent $\frac{1}{n}$ is small at room temperature, and the adsorption isothermal rises correspondingly steeply and bends round sharply (cf. p. 115 and Fig. 23). A small adsorption exponent of course causes a sharp bend in the adsorption isothermal. Hence at very low pressures the amount adsorbed in equilibrium is still appreciable.

The taking-up of gases by metals is a matter of great complexity. Adsorption plays a part, but probably not a decisive one. The fixation of hydrogen by palladium at intermediate and low temperatures appears, accord-

[1] Ann. d. Physik (4), **41**, 289 (1913).

[2] See *Henning*, "Der Geruch," Leipzig, J. A. Barth, 1916, p. 314 *et seq.* The experiments of *Zwaardemaker* and *Hermanides*; also *Kisskalt* [Arch. f. Hygiene, **17**, 380 (1909)]. Also in the action of odoriferous substances on the mucous membrane of the nose, an adsorption appears to be important (see *Henning*, "Der Geruch," p. 375 *et seq.*). The smell of clays and kaolins also depends upon such adsorbed substances [*Rohland*, Zeitschr. f. physiol. Chemie, **59**, 325 (1909); **81**, 200 (1913)].

ing to Valentiner [1] and Holt,[2] to be a sorption in the true sense of the word, i.e. adsorption and subsequent solid solution. This is supported on the one hand by the great increase in the amount taken up at low temperatures, as shown by Valentiner, and further by the fact that the adsorption isothermal holds for low pressures. Holt and his co-workers point out that the Pd as a rule contains both crystalline and amorphous constituents, and that the amorphous are particularly important for the fixation of hydrogen. It is they that chiefly adsorb the gas, and they also bring about the solution in the crystalline portion, without a very different solubility in the two being necessarily implied. Holt and his collaborators further show that the fixation occurs quickly in the first period of time, then slowly, exactly as in the case of the sorption of hydrogen by charcoal described on p. 109; even the noteworthy experiment of McBain described upon p. 109 could be repeated with Pd; Pd superficially saturated with H_2 at first gives off H_2 on evacuation, which is then gradually taken up again, because diffusion of H_2 into the interior of the Pd sets in. At higher temperatures, at which the fixation falls off remarkably, and fairly suddenly—this happens chiefly above 100°—solution must, according to Sieverts,[3] be chiefly responsible for the fixation. Firth [4] actually wishes to assume adsorption alone below 0°, absorption alone above 150°, and sorption only in the intermediate range of temperature. That hydrogen, as compared with other gases, takes up an exceptional position towards palladium, does not tell against the adsorption view. If adsorption depends upon the still unsaturated part of the chemical attractive forces projecting from the surface (see p. 122), the possibility of a specific affinity has certainly to be taken into account in adsorption.

Acetylene is also taken up freely by platinum black.[5] This is, apparently, in the first place, an adsorption accompanied, however, by chemical processes, particularly polymerization and oxidation by oxygen which may be present; the process only slowly approaches an end point; the polymerization products may be directly detected, and in the case of palladium black containing O_2, the C_2H_2 is ignited upon addition.

As regards the interaction of platinum and hydrogen, the slight fixation of H_2 by compact platinum is, according to Sieverts,[6] to be regarded as solution, which view is supported by the positive temperature coefficient. On the other hand, in the fixation of H_2 by platinum black,[7] adsorption should play a large part.

Oxygen appears to be bound by platinum in the true chemical sense, or, in other words, the chemical forces act here with their principal valencies. This is especially supported by the fact that the metal containing oxygen dissolves in acid in proportion to its oxygen content; the temperature coefficient of the fixation is positive, and O_2 cannot be pumped off at ordinary temperatures.[8]

[1] Ber. d. deutsch. physik. Ges. **13**, 1003 (1911).

[2] *Holt, Edgar,* and *Firth* [Zeitschr. f. physik. Chemie, **82**, 513 (1913)]; *Andrew* and *Holt* [Proc. Roy. Soc. **89**, A, 170 (1913)]; *Holt* [*ibid.* **90**, A, 226 (1914)].

[3] Zeitschr. f. physik. Chemie, **88**, 103, 451 (1914).

[4] Journ. Chem. Soc. **117**, 171 (1920).

[5] *Paal* and *Hohenegger,* Ber. d. deutsch. chem. Ges. **43**, 2692 (1910); **46**, 128 (1913).

[6] *Sieverts* and *Jurisch.,* Ber. d. deutsch. chem. Ges. **45**, 221 (1912).

[7] For a method of preparing platinum black by reduction of platinum chloride solution with Al-foil, see McDermott, Journ. Amer. Chem. Soc., **32**, 336 (1910).

[8] See particularly *L. Wöhler,* Ber. d. deutsch. chem. Ges. **36**, 3475 (1903). According to *Langmuir* [J. Amer. Chem. Soc. **40**, 1393 *et seq.* (1918)] the fixation of various gases by platinum corresponds to an activity of the main valencies.

The behaviour of the various platinum metals towards H_2 and O_2 is, according to present experience, very different, and for the present no conclusion drawn from one metal can be applied to another.

The fixation of the gases H_2, N_2, and others by metals, such as copper, iron and nickel, at intermediate and higher temperatures, has mainly the character of a solution [1]; Henry's law holds,[2] the temperature coefficient is positive, the size of the surface has no influence, whilst many gases are not taken up at all to a measurable extent (e.g. N_2 and CO_2 by solid or liquid copper, helium and argon by any metal).

During the war adsorption by charcoal was extensively utilized in gas-masks. Poisonous or irritating gases were held back by adsorption, or by reaction with the moisture present in the charcoal. It was essential for the charcoal employed to have a great velocity of adsorption, since the air to be purified was in contact with it only for a short time. Its adsorptive power had also to be great, since only then could one be certain that it would be sufficiently insensitive to water; for it was necessary that the adsorption of the poisonous gas should not be too strongly diminished by the water simultaneously adsorbed.[3]

IV. The Interface Solid—Liquid

The Interfacial Tension between Solid and Liquid

Just as the phenomena at the interface liquid—liquid are very similar to those at the interface solid—liquid, so also do those at the interface solid—liquid resemble those at the interface solid—gas. Here again the distinction between amorphous and crystalline solids must be made. For the estimation of the interfacial tension of many amorphous solids the method of Ignatiew and Berggren (cf. p. 102) should be applicable, but has not yet been tried. In the case of many other amorphous solids and in the case of crystalline ones all methods otherwise applicable for the determination of interfacial tension fail. That the tension exists cannot be doubted. Small crystals are more soluble than large ones. This fact corresponds entirely to the greater volatility of small crystals, and can only be interpreted upon the assumption of an interfacial tension solid—liquid.

The relation first given by Ostwald for the greater solubility of small crystals is completely similar to the formula deduced upon p. 45 for the greater volatility of small drops. Let two spherical particles of an amorphous or regularly-crystalline solid be in solution-equilibrium with a liquid. Let the radii be r_1 and r_2. Let the solubility be so small that van 't Hoff's laws hold; and let the osmotic pressures in equilibrium be P_1 and P_2. Then we can make use of the same argument as on p. 45, only that in the place

[1] See particularly *Sieverts*, Zeitschr. f. physik. Chemie, **60**, 129 (1907); **77**, 591 (1911); *Sieverts* and *Hagenacker*, *ibid.* **68**, 115 (1910); *Sieverts* and *Krumbhaar*, *ibid.* **74**, 277 (1910); *Sieverts* and *Bergner*, *ibid.* **82**, 257 (1913); *Sieverts* and *Hagenacker*, Ber. d. deutsch. chem. Ges. **42**, 338 (1909); *Sieverts* and *Krumbhaar*, *ibid.* **43**, 593 (1910); *Sieverts* and *Bergner*, *ibid.* **45**, 2576 (1912); *Sieverts* and *Oehme*, *ibid.* **46**, 1238 (1918); *Sieverts*, Zeitschr. f. anorg. Chemie, **92**, 329 (1915).

[2] But not in general; in the case of many polyatomic gases the amount taken up is proportional to the square root of the gas pressure; the gas is decomposed into its atoms in the metal.

[3] See on this point also *Bohart* and *E. Q. Adams*, J. Amer. Chem. Soc. **42**, 523 (1920); *Lowry* and *Hulett*, *ibid.* **42**, 1393 (1920).

of the work of distillation we have the osmotic work, and in place of the vapour pressure the osmotic pressure. We have therefore

$$\frac{RT}{M}\log\frac{P_2}{P_1}=\frac{2\sigma}{\varrho}\left(\frac{1}{r_2}-\frac{1}{r_1}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

P_1 and P_2 are proportional to the solubilities L_1 and L_2. If we assume r_1 to be large, that is, ascribe to the solid the usual plane surface, then its solubility is equal to the normal L. For L_2 we can then put L_ω, leave out the suffix of r_2, and thus get the formula

$$\sigma=\frac{RT\varrho r}{2M}\log\frac{L_\omega}{L} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The interfacial tension of a solid may thus be calculated from the increased solubility of small particles of radius r.

W. Ostwald [1] and Hulett [2] have carried out experiments of this kind. The latter found, for example, in the case of gypsum particles, the radius of which was determined by the microscope to be $0{\cdot}3\mu$, a solubility as measured by the conductivity of 18·2 millimol per litre (at 25°), while particles of radius 2μ still showed the normal solubility of 15·3 millimol. According to Kenrick,[3] we can recognize with the Toepler striæ-apparatus how in a saturated solution of gypsum striæ sink downwards from fine gypsum particles, while this is naturally not the case with a large crystal. W. J. Jones [4] recalculated the experiments of Hulett, taking the dissociation into account, and obtained for gypsum a value of 1,050 dyne/cm., and for barium sulphate 1,300 dyne/cm.

These values are greater than those found by Berggren for the surface tension of amorphous solids (cf. p. 102). If we assume such an order of magnitude for the interfacial tension of crystalline solids to be probable, it follows that the influence of σ upon the solubility will only become evident in the case of particles with a radius less than 1μ and will then increase rapidly as the radius decreases, as was already discussed upon p. 46 in dealing with the vapour pressure of small drops.

In the measurement of the E.M.F. of cells, especially with electrodes of the second kind, in which therefore the metal of the electrode is covered with a finely powdered salt, this increased solubility of fine crystals has frequently made itself felt. As examples we have the excessive solubility

[1] *W. Ostwald*, who was the first to deduce this equation [Zeitschr. f. physik. Chemie, **34**, 503 (1900)], writes

$$RT\log\frac{c_2}{c_1}=3\varphi\sigma\left\{\frac{1}{r_2}-\frac{1}{r_1}\right\};$$

here c_1 and c_2 denote the solubilities of the particles, φ the molecular volume, $\frac{M}{\varrho}$ therefore. Between this and the formula given in the text there is a difference in the numerical factor; *Ostwald* has 3 instead of 2. This arises from the fact that in his argument he transforms a number of particles of radius r_1 into particles of radius r_2, and calculates this surface work instead of the work which is gained when a small amount is taken from the first particle and added to the second. The latter mode of considering the problem is, however, the correct one, for only in this case can we regard the solubility of the particles as constant, while in *Ostwald's* case it is variable, and assumes an indeterminate value when the particles disappear.

[2] Zeitschr. f. physik. Chemie, **37**, 385 (1901); **47**, 357 (1904); see also *Kohlrausch, ibid.* **44**, 199 (1903).

[3] J. Phys. Chem. **16**, 516 (1912).

[4] Zeitschr. f. physik. Chemie, **82**, 448 (1913); Ann. d. Physik (4), **41**, 441 (1913).

of very finely divided calomel in the construction of normal electrodes,[1] and that of mercurous sulphate in the construction of standard cells.[2] Here also the size of the particle at which the phenomenon becomes evident appears to be about 1μ. As we should expect, the metallic electrode coated with finely powdered salt is positive towards that coated with coarse salt. The change of the fine-grained salt into the coarse proceeds very slowly, so that it does not apparently take place spontaneously without the introduction of coarser crystals.

Upon the increased solubility of strongly-curved boundary surfaces depends perhaps the increased reactivity of finely powdered substances. Podzus [3] has recently described experiments of this kind: Al_2O_3, ZrO_2, ThO_2, which had been powdered to 1μ grain, dissolved up to several per cent. in concentrated HCl, while they were practically insoluble in the form of large pieces. In opposition to Podzus' opinion, there appears to me to be no reason at present for ascribing an especial increase in reaction velocity to fine powders. The increase in solubility appears to me to be sufficient explanation. Moreover, it has long been a matter of laboratory experience that even extremely slowly reacting solids may be made to react if they are carefully ground very fine; we have to go down to a grain of about 1μ to attain this increased reactivity.

The question as to the significance of the interfacial tension of crystals for their equilibrium with saturated solutions has been much discussed. Gibbs[4] first developed the following theory. He ascribes to each crystal face a characteristic interfacial tension, and arrives at the condition for equilibrium that the sum of the free surface energies $\Sigma\sigma\omega$ must be a minimum for a constant volume in equilibrium. He calculates also the amount of free surface energy which must be added to the thermodynamic potential when a crystal face is displaced a certain amount by growth. As Valeton [5] points out, the interfacial tension comes into question practically only in the equilibrium of very small crystals, beginning to make itself felt as soon as the solubility begins to be sensibly influenced by the interfacial tension; after what we have just said, this is the case, in view of the most probable values of the interfacial tension, for crystals below a diameter of 2μ. In the case of larger crystals other influences, according to Valeton, predominate, especially the velocity of crystallization; so that for these the above-named Gibbs boundary condition is not in reality fulfilled (cf. p. 335). Matters are not therefore as Curie [6] supposed, who arrived in a different manner at the same condition for equilibrium as Gibbs. Curie believed that it also held in practice for macroscopic crystals, and that a crystal can change its shape as required by the theory, by one face growing and another diminishing. This is not the case, as Valeton showed by experiments with alum crystals; the various faces of a macroscopic crystal have the same solubility, and the above-mentioned equilibrium condition only becomes important, even practically, for microscopic and ultra-microscopic crystals.

[1] *Sauer*, Zeitschr. f. physik. Chemie, **47**, 160 (1904).

[2] *v. Steinwehr*, Zeitschr. f. Elektrochemie, **12**, 578 (1906); see further *Allmand*, Journ. Chem. Soc. **95**, 215 (1909); **97**, 603 (1910); Zeitschr. f. Elektrochemie, **16**, 254 (1910).

[3] Zeitschr. f. physik. Chemie, **92**, 227 (1917).

[4] P. 314 *et seq.*, especially also note p. 325 of "Scientific Papers," Vol. I.

[5] Verh. d. Sächs. Akad. d. Wiss, math.-phys. Kl. **67**, 1 (1915); further also Physik. Zeitschr. **21**, 606 (1920).

[6] Bull. Soc. min. de France, **8**, 145 (1885).

Ehrenfest [1] doubts, probably rightly, whether the general conditions of equilibrium for a crystal can be deduced without using molecular-kinetic considerations, and points out that, whether or no, with Brillouin,[2] Pawlow,[3] and others, we must introduce, besides the free surface energy of the crystal faces, free edge- and corner-energies, it depends upon the size of the radius of molecular attraction.

Wetting and Displacement of Liquid

The interfacial tension of a solid against a pure liquid is important for the phenomena of wetting and of displacement of one liquid by another. These phenomena are largely similar to the phenomena of spreading discussed on p. 96, with this difference, that in place of one of the liquids we have a solid. Since we cannot in general measure the interfacial tension of a solid against a gas or liquid, we do not arrive at quantitative relations, but we do obtain qualitative ones, which are of importance for many phenomena.[4]

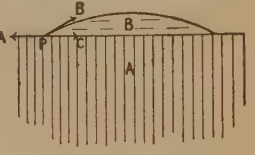


Fig. 28.

Let σ_{fg} be the surface tension of the liquid, σ_{sg} that of the solid, σ_{sf} the interfacial tension of the solid against the liquid. If now we have a drop of liquid upon a solid surface, at a point P three forces act as represented in Fig. 28. We have to take three possibilities into account (cf. p. 96), namely:

1. The drop remains lying in equilibrium upon the solid surface with formation of an angle of contact α; then

$$\sigma_{sg} = \sigma_{fg} \cos \alpha + \sigma_{sf}$$

or

$$\sigma_{sg} - \sigma_{sf} = \mathrm{j} = \sigma_{fg} \cos \alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The difference between the interfacial tensions of the solid, which may be described as the *adhesion tension* (Haftspannung), is equal to a fractional part, given by the cosine of the angle of contact, of the surface tension of the liquid. The fraction can be positive or negative according as α is an acute or obtuse angle; the limit of complete non-wetting is an angle of 180°.

2. The drop spreads over the solid surface, complete wetting ensues. Then $\alpha = 0$. Therefore either

$$\sigma_{sg} = \sigma_{fg} + \sigma_{sf} \text{ or } \sigma_{sg} - \sigma_{sf} = \mathrm{j} = \sigma_{fg} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or, since the magnitudes of the three tensions are independent of one another,

$$\sigma_{sg} > \sigma_{fg} + \sigma_{sf} \text{ or } \sigma_{sg} - \sigma_{sf} = \mathrm{j} > \sigma_{fg} \quad . \quad . \quad . \quad . \quad (3)$$

In the case of complete wetting, the adhesion tension is equal to or greater than the surface tension of the liquid.[5]

[1] Ann. d. Physik (4), **48**, 360 (1915); there also further literature.

[2] Ann. de chim. et de phys. (7), **6**, 540 (1915).

[3] Zeitschr. f. Kristallogr. **40**, 189 (1905); **42**, 120 (1906); Zeitschr. f. physik. Chemie, **72**, 385 (1910).

[4] See particularly *Quincke*, Wied. Ann. **2**, 145 (1877).

[5] *Röntgen* [Wied. Ann. **3**, 324 (1878)] and Tangl [Ann. d. Phys. (4), **34**, 311 (1911) and 42, 1221 (1913)] made experiments in order to measure the adhesion tension $\mathrm{j} = \sigma_{sg} - \sigma_{sf}$ directly. They determined it under certain assumptions, by taking a rubber diaphragm—once in air and once in water—and deforming it measurably by known pressures. By coating the rubber with a thin layer of metal or paraffin, they tried also to measure an adhesion tension for the latter substances. At present various possibilities of error make the results uncertain; but they indicate that the angle of contact in these cases is practically zero.

3. Or, finally, the drop remains lying on the surface without spreading, the surface is unwettable. No surface is formed with the interfacial tension σ_{sf}, but instead, the boundaries with the tensions σ_{fg} and σ_{sg} are preserved. Then the free energy of the surface of the liquid against the solid must be greater than the sum of the free surface energies of the liquid and the solid against the gas, or

$$\sigma_{sf} > \sigma_{fg} + \sigma_{sg} \text{ or } (\sigma_{sg} - \sigma_{sf}) = -\mathrm{j} > \sigma_{fg} \quad . \quad . \quad . \quad . \quad (4)$$

If the adhesion tension, taken as negative, is greater than the surface tension of the liquid, then we have no wetting.

Fig. 29 represents the various limiting cases plainly; for the sake of simplicity, only σ_{sg} is taken as variable. We see from it in the first place that liquids in general wet the better the lower their surface tension. This we know to be borne out by experience; liquids with a small surface tension such as ether, alcohol, and generally the majority of organic liquids, wet most solid bodies better than water or sulphuric acid, and these again

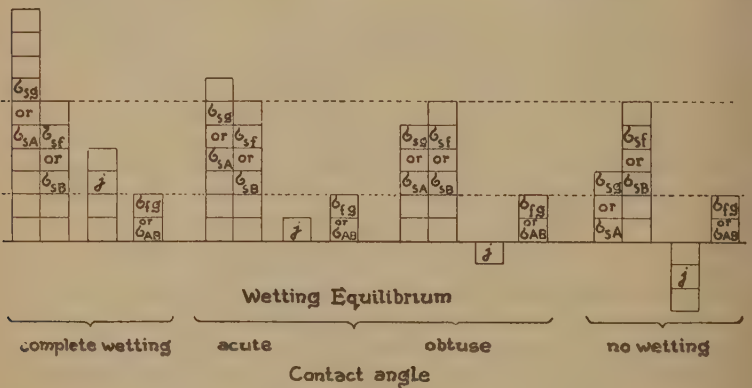


Fig. 29.

better than mercury or molten metal. A small value of σ_{sf} is also favourable to wetting. In the cases in which water wets more easily than an organic liquid, we are probably dealing with low values of the interfacial tension of the solid substance in question against water.

Waxed, polished or smoked metal plates are surfaces which are completely unwettable by water. Instead of smoking the plates, they may be coated with As_2O_3 by bringing them into the flame of burning arsine (AsH_3).[1] Also the leaves of many plants (cabbage, mimosa) are not wetted by water, a circumstance which must be taken into account in spraying as a defence against plant-pests.

In place of the competition of a gas and a liquid for the surface of a solid, which we meet in the case of wetting, we have in the displacement of one liquid by another the competition of two liquids for the surface of a solid. The same considerations hold as have just been put forward, except that we must introduce in place of gas and liquid two liquids A and B. More important than the case in which the liquids spread out upon a large solid

[1] See *Ollivier*, Ann. de chim. et de phys. (8), **10**, 269 *et seq.* (1907).

surface is the case in which the solid is in the form of fine powder in a system of two not completely miscible liquids; the powder may then either enter one or the other of the liquids, or remain at the interface. Following des Coudres,[1] we may put the argument, which is entirely unaltered in essentials, as follows. Let a small cylinder of the solid of sectional area ω be just at the interface of the two liquids as shown in Fig. 30A, and let the work K be required to move the cylinder through the distance x to a position (Fig. 30B) in which it is completely surrounded by liquid B. This work is done against the interfacial tension forces, and amounts to

$$\omega\sigma_{sA} - \omega\sigma_{sB} - \omega\sigma_{AB},$$

for an area ω of the interface and a tension σ_{sA} disappear, and two new

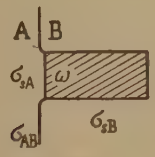


Fig. 30A.

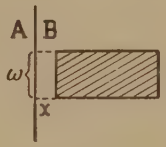


Fig. 30B.

surfaces, each of area ω, appear instead, the one with tension σ_{sB} and the other with tension σ_{AB}. Hence

$$\sigma_{sA} - \sigma_{sB} - \sigma_{AB} = \frac{Kx}{\omega}.$$

If

$$\sigma_{sA} \gtreqless \sigma_{sB} + \sigma_{AB} \text{ or } \sigma_{sA} - \sigma_{sB} = j \gtreqless \sigma_{AB}. \quad . \quad . \quad . \quad . \quad (5)$$

then $\frac{Kx}{\omega} = 0$ or is positive; no work has to be done, or work is gained as the case may be, when the solid passes into liquid B; it is surrounded by it spontaneously. This corresponds in the case of wetting to the spreading of the liquid upon the solid.

The converse case is quite symmetrical—case 3, corresponding to equation (4)—that is, complete surrounding by liquid A:

$$\sigma_{sB} \overset{=}{>} \sigma_{sA} + \sigma_{AB} \text{ or } \sigma_{sB} - \sigma_{sA} = -j > \sigma_{AB} \quad . \quad . \quad . \quad (6)$$

Between these two limiting cases we have the case of equilibrium with a definite contact angle [corresponding to case 1, equation (1)]:

$$\sigma_{sA} = \sigma_{AB}\cos\alpha + \sigma_{sB} \text{ or } \sigma_{sA} - \sigma_{sB} = j = \sigma_{AB}\cos\alpha \quad . \quad . \quad (7)$$

The powder adheres to the interface and is partly coated by A and partly by B.

F. B. Hofmann[2] has thoroughly investigated these phenomena by allowing powders of various solids to distribute themselves between water and an organic liquid (ether, chloroform, isobutyl alcohol, benzene, xylene, isoamyl alcohol, paraffin oil); instead of the powder, larger scales of the solid were also employed (small glass plates, lamellæ of molybdenum

[1] See *Rhumbler*, Arch. f. Entwicklungsmechanik, **7**, 225 (1898); for a somewhat stricter argument see *Hofmann*, Zeitschr. f. physik. Chemie, **83**, 389 *et seq.* (1913).

[2] Zeitschr. f. physik. Chemie, **83**, 385 (1913).

sulphide). The results were fundamentally in agreement with theory. A number of solid substances, such as gypsum, glass, etc., always passed preferentially into the water; they may be termed *hydrophilic*. Others, such as sulphides (MoS_2, PbS, HgS, etc.), oxides (Pb_3O_4, Fe_3O_4, HgO, etc.), halides (AgI, HgI_2, PbI_2, etc.), and carbon remained in all cases more or less adhering to the interface. They belong therefore to the first or third case; they are either completely enveloped by the organic liquid, or there exists an equilibrium between the two liquids with formation of a contact angle. These solid substances are therefore *hydrophobic*. Gypsum may be taken as a decidedly hydrophilic, and molybdenum sulphide as a decidedly hydrophobic, substance.

The differences between the various organic liquids are, according to the experiments of Hofmann, not so great, although hydrocarbons, such as paraffin oil and petroleum, belong to the strongly wetting liquids, so that they wet glass as easily as water does; on the other hand, in the case of ether and chloroform, the easier wetting of glass by water is quite evident.

The definiteness of such experiments suffers from the fact that the final states of equilibrium are not set up immediately and without special precautions; the previous treatment of the solid surface is of decisive importance. The following example from Hofmann may be given. Glass is certainly more easily wetted by water than by petroleum when equilibrium is set up; if sufficient time is allowed, petroleum is always finally displaced by water. If now we pour petroleum into a clean, air-dry test-tube, it will still, after some seconds, be so completely displaced by water that the latter forms a perfectly continuous coating round the glass. The petroleum has not had time to displace the air from the surface, and the water can wet the glass straight off, because it has only to displace air and not petroleum. But if the petroleum has been in contact with the walls of the glass for only half a minute before the water is poured in, then it is not always possible to get a complete coating of water; the characteristic ragged patches which indicate partial wetting, remain; and if the petroleum has been in contact with the glass for several minutes, water at first does not adhere to the glass at all, but a smooth coating of petroleum remains, and only after about a minute does the water again commence to adhere to the glass. This is due to the fact that the low solubility of petroleum in water prevents the thinnest film from being easily removed. It is the same phenomenon as is observed in the case of the spheroidal state of a gliding drop upon a liquid (cf. p. 101). That the length of time during which the petroleum is in contact with the glass has some influence is probably due to the slow displacement of the last traces of air by the petroleum, which fills up deeper and deeper pores and scratches.[1]

As Rhumbler[2] has shown, displacement is of importance in many biological phenomena. We must, however, always take account of the fact that in the case of vital processes an interfacial tension may be changed by internal variables without any action from outside; thus the interfacial tension between a naked amœba and the surrounding water can change on

[1] The distribution of a powder between two liquids depending upon displacement corresponds to the floating of a heavy powder upon the surface of a liquid, which depends upon the particles not being wetted. *Valentiner* [Physik. Zeitschr. **15,** 425 (1914)] was able to show that a powder actually does float the more easily the greater its angle of contact (see note, p. 161).

[2] Arch. f. Entwicklungsmechanik, **7,** 103 (1898); **30,** 194 (1910); Ergebn. d. Physiologie, **14,** 576 (1914); see also *Friedemann* and *Schönfeld,* Biochem. Zeitschr. **80,** 312 (1917).

account of processes which go on within its protoplasm without external influence. But the taking-up and ejection of solid bodies by amœbæ is apparently entirely controlled by the fact that when the protoplasm of the amœba takes up the solid, the surrounding water is displaced from the solid, while when it is ejected, it adheres to the interface, or the protoplasm is displaced by water. Just as an alga-thread can be rolled up in an amœba, so can a shellac thread be rolled up under water by a drop of chloroform; if we take a thin glass thread which is coated with shellac, and is longer than the drop of chloroform, and bring it into contact with the latter, it is at first taken up, since the water is displaced by the chloroform from the shellac surface; the shellac, however, then dissolves in the chloroform, and the thread of glass is rejected, since the chloroform is displaced from the glass by the water.

Upon this phenomenon further depends the construction of the shells of shell-bearing amœbæ.[1] The protoplasm protruding from the shell contains small fragments of building material (grains of quartz, etc.) previously taken up, which when protrusion takes place reach the interface owing to a change in the hydrophily of the protoplasm, and are there consolidated to the shell by a liquid binding material simultaneously secreted. This process may also be imitated by bringing finely-powdered hydrophilic solids, such as quartz or glass, into an oil, such as castor oil, and pressing the mixture from a syringe into a suitable liquid, such as 70 per cent. aqueous alcohol. The expressed drop of castor oil surrounds itself with a shell of fine quartz or glass powder, which is strikingly like the amœba shell.

These phenomena of displacement and wetting have also technical importance. Upon them depends the treatment of ores by the so-called flotation method, to which belong the Elmore, Cattermole, and other processes.[2] If we have a mixture of hydrophobic ore (sulphides, etc.) with hydrophilic gangue (quartz and the like), they can be separated to a considerable extent in the following manner. The finely-powdered ore is introduced into water which is covered by a layer of oil—mineral oil is usually employed; by blowing in air or generating CO_2 a strong froth is

[1] *Rhumbler*, Arch. f. Entwicklungsmechanik, **7**, 239 *et seq.*; Ergeb. der Physiologie, **14**, 587 *et seq.* (1914).

[2] See *Hoover*, "Concentrating Ores by Flotation," London, 1912; *Vageler*, "Die Schwimmaufbereitung der Erze," Dresden, 1913; *Rickard*, "Concentration by Flotation," New York, 1921; *Glatzel*, "Ein Beitrag zum *Elmoreschen* Extraktionsverfahren," Diss., Dresden, 1908; *Moldenhauer*, "Der *Elmore*-Vakuumprozess," Diss., Breslau, 1915; Kolloidzeitchr. **13**, 229 (1913); *Vageler*, Metall und Erz, **17**, 113 (1920). Long before the *Elmore* method, as *Nathansohn* pointed out, graphite had been separated from earthy impurities by a flotation method (German patents of the brothers *Bessel*, Nr. 42, Class 22, 1877; Nr. 39,369, Class 22, 1887). (Although the flotation process is of enormous industrial importance, and its basic principles of great scientific interest, the literature on the subject is sparse to a degree, owing to the fact that the large financial interests concerned have pursued a policy of concealment. Hoover's book is the only one of any value, but attention should be drawn to a paper by *Sulman* [Trans. Inst. Mining and Met. **29**, 44 (1920)], one of the chief workers in this field, which aims at giving a capillary chemical explanation, and at the same time advocates the existence of a true contact angle and of a new property, the "hysteresis of contact angle," and supports this view by very interesting experimental data. *Edser*, in the "Fourth Report on Colloid Chem.," [H.M. Stationery Office, London, 1922], also gives a very useful account of both theory and practice. Recently almost ash-free coal has been obtained by flotation, yielding a new coke of extraordinary properties [*Bury*, *Broadbridge*, and *Hutchinson*, Trans. Inst. Min. Eng. **60**, 243 (1921)]. It should be added that a great deal of published practical data exists. [Trans.]).

produced, which contains the oil and the hydrophobic ore particles sticking to the oil, while the hydrophilic gangue remains in the water. The frothing serves the purpose of saving oil by developing as large a surface as possible, for the oil can produce its effect in an extremely thin layer. Wetting and displacement are, however, only the fundamental phenomena in this process. Along with them, capillary-electrical and colloido-chemical influences, such as the size of grain and coagulation, play an important, if still very obscure, part.

The question whether a partial wetting and displacement occur as a state of equilibrium with formation of a definite contact angle, is really still an open one. The contact angle is, of course, often enough observed [1]; but an example is still wanting in which this contact angle fulfils the conditions which it would have to fulfil if it corresponded to a state of equilibrium; it should not only show a given invariable value, but the point at which the three interfaces meet at the definite contact angle should be easily movable, and should establish itself reversibly at the correct value of the angle, as the meniscus does in a well-wetted tube.[2] This rarely, if ever, happens, since small changes and impurities in the surface suffice to influence the contact angle strongly. According to the experiments of A. Pockels,[3] the following results seem to be reliable. Upon glass or platinum which is as clean as possible, water, glycerine, ethyl alcohol, oil of turpentine, and petroleum have a contact angle of zero; ether, benzene, carbon disulphide, oils, oleic acid, show contact angles. That of benzene on glass was found with fair constancy to be 6°; those of Provence (olive) oil and oleic acid were found to be large (about 30°). Ice is completely wetted by water, petroleum, and carbon disulphide; oil and oleic acid form contact angles. Coal (anthracite and others) is wetted by benzene and petroleum; water gives a contact angle.

Even the adsorption of air appears to suffice to change the angle of contact considerably. At any rate, according to Miss Pockels, this is the best explanation of the fact that upon a platinum foil carefully cleaned by ignition, upon which water at first had a zero contact angle, a distinct contact angle appeared in 10 minutes, and a considerable one after 30 minutes' exposure to air; in the case of glass this happened only after 3 and 24 hours respectively. It is probable that the air is more strongly adsorbed upon the metal than upon glass.

Distinct contact angles of a regular character were apparently earliest observed upon freshly generated surfaces. Thus Möller [4] found that electrolytically generated hydrogen bubbles rest upon mercury or other carefully cleaned metallic electrodes with a definite contact angle, which depends in a regular manner upon the electrical polarization and the temperature, and can be brought into relation with the over-voltage (cf. p. 301).

Rhumbler [5] describes how, in the case of the shell-formation of amœbæ, the freshly extruded protoplasm comes into contact with the shell-wall at a definite contact angle and solidifies there to a new shell-wall.

Moser's [6] breath-figures also depend upon differences in the angle of

[1] See especially *Quincke*, Wied. Ann. **2**, 145 (1877); and *Sulman*, *loc. cit.* p. 161.
[2] *Volkmann*, Wied. Ann. **53**, 662 (1894).
[3] Physik. Zeitschr. **15**, 39 (1914).
[4] Ann. d. Physik (4), **25**, 725 (1908).
[5] Ergebn. d. Physiologie, **14**, 507 *et seq.* (1914). There is also other literature.
[6] Pogg. Ann. **56**, 177 (1842); **57**, 1 (1842); *Waidele*, Pogg. Ann. **59**, 255 (1843).

contact. The drops produced by the breath on a glass plate have a quite different appearance at greasy than at clean parts of the plate ; in the one case we have the well-known irregular, ragged edges ; in the other, regular edges or complete wetting. The persistence with which a finger-print, for example, upon a glass plate resists even vigorous cleaning is curious. This probably depends upon the fact [1] that, as already mentioned on page 160, the impurities also penetrate more deeply into the pores and are difficult to remove.

In order to test how far a solid surface is clean or contaminated with oily impurities, a suitable method, according to Miss Pockels,[2] is to dip the object into a pure water-surface and to see if an adsorption layer, a " solution current " (cf. p. 98), proceeds from it. It is therefore dipped into a water surface which is covered with carefully ignited charcoal powder, talc, or the like ; if the powder retreats from the solid, if, that is, an adsorption layer is formed, then it is contaminated. If it is clean, then the liquid with the powder moves towards it, which on account of viscosity must be the case when a solid is dipped into a liquid.

The Adsorption of Vapours

In the adsorption of vapours close to the saturation pressure, wetting must be taken into account. The argument on p. 124, in which the surface of the adsorbent is covered with a layer of liquid during the adsorption of a gas below the critical temperature postulates the wetting of the adsorbent by the liquid. If the liquid to which the gas is condensed does not wet the adsorbent (or only with formation of a contact angle), then we may not assume, in the range of low pressures considered on p. 123, a layer of liquid, but only a layer of compressed vapour. The adsorption isothermal will be valid whether the liquid separating from the vapour wets the adsorbent or not ; for it is also valid above the critical temperature. The validity of the adsorption isothermal for dilute vapours has only been examined for the vapours of wetting liquids. But there can be no doubt that it would also be valid for vapours of non-wetting liquids.

As we approach the saturation pressure, the state of affairs in the case of the vapours of wetting liquids will be as follows. The higher the pressure, the thicker will be the film of liquid contained in the adsorption layer.[3] The adsorption isothermal becomes bent and approaches adsorption-saturation. At the pressure corresponding to the saturation of the vapour, a finite amount of liquid separates for an infinitely small increase in pressure, $\frac{da}{dp}$ is infinitely large. The adsorption isothermal, therefore, ascends vertically at that point, and will previously change its course from the horizontal saturation line along a turn which brings it into the vertical, as shown by curve 1, Fig. 31. This corresponds to the adsorption isothermal of water on cotton, according to Orme Masson.[4]

In the case of adsorption of a vapour of a non-wetting liquid, the adsorption exponent $\frac{1}{n}$ will be greater than that for a wetting liquid, since the vapour behaves like a gas above the critical point. There is less tend-

[1] See on this point *Rayleigh*, Nature, **86**, 416 (1911) ; *Aitken*, *ibid.* p. 516.
[2] Ann. d. Physik (4), **8**, 854 (1902).
[3] Even *Langmuir* (*loc. cit.* p. 123) reckons in the neighbourhood of saturation with a considerable number of layers of molecules.
[4] *Orme Masson* and *E. S. Richards*, Proc. Roy. Soc. **78**, A, 412 (1907).

ency towards an adsorption saturation, and the possibility exists th supersaturation continues above the saturation pressure and that only whe this supersaturation is removed by suitable nuclei for condensation in t surface will the liquid condense in drops upon the surface; the vertic rise of the adsorption isothermal then takes place. In the extreme case should have a curve of the kind of 2 in Fig. 31; and in every case one whi runs below curve 1, and has a rapid rise only just before saturation pressu

If we examine these phenomena not isothermally, but in the field temperature, we see that in the case of a wettable surface the dew-point the temperature at which vapour condenses on the surface—lies above t saturation temperature, since the surface is already covered by a film liquid above this temperature. In t

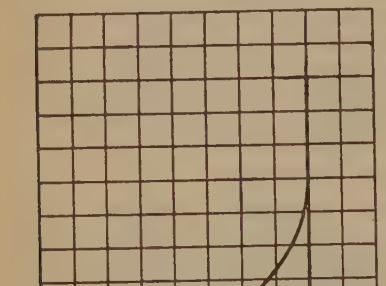


Fig. 31.

Absorption Isothermals of a Vapour on a wettable and a non-wettable Surface.

case of the vapour of a non-wetti liquid, on the other hand, the de point lies below the saturation temper ture; a supersaturation of the vapo can be brought about. Cantor [1] w in fact, able to show that upon petroleum surface water first conden in drops at a temperature sensib below the saturation-point. Betwe a non-wettable liquid surface and t non-wettable surface of a solid th is of course no fundamental differe in this respect.

The complete adsorption isoth mal of a vapour upon a non-wetta surface has not yet been measured, b in many cases complete isotherm have been measured for wettable s faces; for example, the taking-up water by cotton, glass wool, carb silicic acid gels, etc. The majority these examples do not quite correspo to the simple case represented curve 1, Fig. 31. For the adsorb is, in the case of charcoal, silicic a gels, and so on, to be regarded as a colloidally disperse solid foam, and t causes the filling up of the ultra-microscopic capillary spaces by the liqu which takes place even at pressures below the saturation pressure p. 663). Although these relations can only be discussed later when deal with gels, it is advisable partially to anticipate them here, as far as influence of the ultra-microscopic capillary spaces is not sensible. Si this only makes itself felt in the case of very fine capillary spaces, we m very well put forward gels with coarse capillaries, such as cotton, e as simple examples of complete adsorption isothermals of satura vapours. As has been said, the taking-up of water by cotton and by not highly dried glass wool follows to a great extent the behaviour represen by curve 1, Fig. 31.

For the steep part of this isothermal, which is convex towards the axi p, a number of regular relations hold, to which Trouton [2] in particular

[1] Wied. Ann. **56**, 492 (1895).
[2] *Trouton* and *Poole*, Proc. Roy. Soc. **77**, A, 292 (1906).

called attention. This part of the curve is approximately parabolic, and may be represented by the equation

$$\frac{(a_s - a)^2}{100 - \frac{p}{p_s}} = \text{Const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here p_s and a_s are the saturation pressure and the amount adsorbed at saturation.

More important is the dependence of the adsorption upon temperature in this region. The Clapeyron-Clausius argument leads, when applied (as on page 135 to the isosteres), to

$$\frac{(v_2 - v_1)\delta p}{w q_a} = \frac{\delta \mathrm{T}}{\mathrm{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here $v_2 - v_1$ is the increase in volume when the quantity w of water evaporates from the adsorbent. According to Boyle's law,

$$w = \frac{p}{p_s} \varrho_s (v_2 - v_1),$$

where p_s is the saturation pressure and ϱ_s the vapour density at saturation. Hence

$$\frac{\delta p}{\delta \mathrm{T}} = \frac{p}{p_s} \frac{\varrho_s q_a}{\mathrm{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For saturation pressure we have correspondingly

$$\frac{\delta p_s}{\delta \mathrm{T}} = \frac{\varrho_s q_a}{\mathrm{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

if we assume that q_a has practically the same value. This is permissible, since according to page 136 the heat of adsorption changes greatly with the amount of water taken up only at low pressures but not at high. From equations (3) and (4) it then follows that

$$\frac{\delta p}{\delta \mathrm{T}} = \frac{p}{p_s} \frac{\delta p_s}{\delta \mathrm{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The integration of equation (5) shows that $\frac{p}{p_s}$ is constant. The isosteric p, T curves here considered are not only *isosteric* curves, as proper to equal amounts adsorbed, but also at the same time *isohygrometric* curves, as Trouton and Miss Poole [1] call them; that is, the same amount adsorbed corresponds at various temperatures to a constant fraction of the saturation pressure. Isosteric and iso-hygrometric curves coincide.[2]

This relation is, as Trouton [3] points out, important for the theory of the hair and catgut hygrometer. Hair and catgut behave like cotton as regards the adsorption of water vapour. The relation deduced will there-

[1] Proc. Roy. Soc. **77**, A, 292 (1906).

[2] *Trouton* points out the curious circumstance that the vapour-pressure isothermal of an aqueous sulphuric acid solution, in which the H_2SO_4 plays the part of the adsorbent, resembles the complete adsorption isothermal, and that here also the isosteric curves—vapour pressure/temperature curves, with H_2SO_4 unchanged in amount—coincide with the isohygrometric—vapour pressure/temperature curves, the vapour pressure being a constant fraction of the saturation pressure. A behaviour of this kind is intelligible if the attractive force which binds the water to the cotton is not fundamentally different from that which binds the water to the sulphuric acid molecule (cf. p. 671).

[3] *loc. cit.* p. 164.

fore also hold for them. From this it follows that a definite hygroscopicity, that is, a definite relative pressure of water vapour, corresponds to a definite amount of moisture taken up by the hair or catgut, independently of the temperature. If the amount of moisture taken up is connected definitely with a change of length, the hygrometer correctly registers the moisture independently of the temperature.

In the adsorption of water by glass wool we have an example, although not a perfect one, of the adsorption of vapour at a non-wettable surface, which however passes over by the action of water into one more easily wetted. If glass is heated at high temperatures (150° and over) with drying-agents, or even with water, it becomes difficultly wettable. This disappears again, if the glass stands for some time in contact with water at ordinary temperatures.[1] This behaviour probably depends upon the fact that the uppermost layer of glass, which is easily wetted, imbibes water and therefore consists of a silicic acid gel containing alkali. When heated in presence of P_2O_5 this skin of gel is dried up, and scales off; upon heating with water it is dissolved away, without the surface of glass beneath it imbibing water at the higher temperature, while at ordinary temperatures a silicic acid gel is re-formed upon the surface.

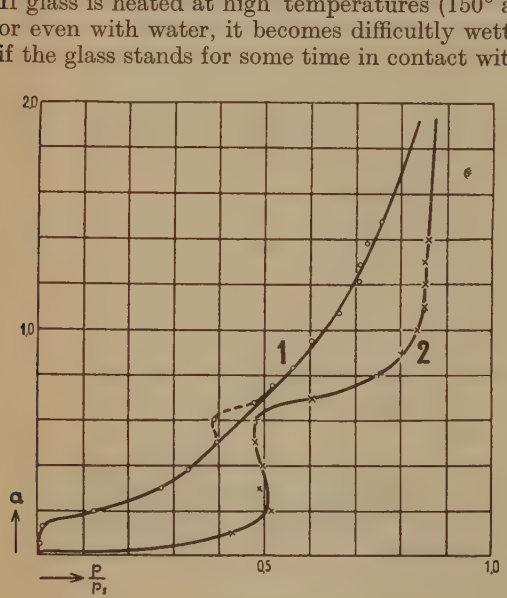


Fig. 32.—Adsorption Isothermals of Water on a weakly (1) and a strongly (2) dried Glass Wool.

Now Trouton [2] found a remarkable difference between the behaviour of glass wool which had been dried by P_2O_5 at ordinary temperature for as short a time as possible, and glass wool which had been heated at 162° in a vacuum over P_2O_5. Curve 1, Fig. 32, gives the adsorption isothermal of the slightly dried glass wool; curve 2, that of the wool heated and dried *in vacuo*; the abscissæ are the relative water-vapour pressures, the amounts adsorbed are given in a relative measure. The first is not fundamentally different from that of an easily wettable adsorbent, such as cotton (curve 1, Fig. 31). Curve 2, Fig. 32, on the other hand, corresponds at low pressures to the adsorption isothermal of a badly wettable surface, inasmuch as a much smaller amount is adsorbed, since in the adsorption layer a film of liquid is not present. Then there appears at a certain pressure an actual supersaturation effect; the amount adsorbed increases greatly, while the pressure decreases. It is as if nuclei had been formed, so that water could separate at the surface. This now soon causes imbibition of water by the external layer of the glass, and hence a further course of the adsorption isothermal which passes over into that of the slightly dried wool. Since Trouton's

[1] *Volkmann*, Wied. Ann. **53**, 646 (1894).
[2] Proc. Roy. Soc. **79**, A, 383 (1907).

experiments were carried out without taking the wettability into account, a comparison of the adsorption isothermals of glass surfaces having a known wettability would not be without importance.

The adsorption of the vapours of a number of organic liquids up to pressures approaching that of the saturated vapour was measured by G. C. Schmidt and Hinteler.[1] The usual isothermal was valid to a great extent. Adsorption saturation was not well marked. The sharp rise usually took place immediately on reaching the pressure of the saturated vapour.

The measurement of adsorption near, and at, the saturation pressure is beset with considerable difficulties. To spread out the adsorbent in a desiccator, on the bottom of which is a solution having the required vapour pressure, is by no means a certain method. Strict constancy of temperature and uniformity of pressure in the whole space inside the desiccator are not at all easy to obtain. It is safer to ensure that the adsorbent is surrounded as far as possible by the liquid having the required vapour pressure. Thus the following arrangement used by Orme Masson [2] may be recommended. The adsorbent is contained in a clay cylinder, which is completely immersed in the liquid of the required vapour pressure; the liquid is able to diffuse slowly through the pores into the interior of the cell. In the case of adsorbents such as cotton, it is convenient to wind them round the bulb of a thermometer, which dips into the interior of the clay cylinder (cf. p. 672).

The ubiquitous presence of water vapour implies that practically all solid surfaces of the objects around us are coated with a film of adsorbed water. E. Warburg and Ihmori [3] determined it for many solid substances by measuring the increase in weight of carefully dried substances when brought into an atmosphere of water vapour, using a very accurate balance. In atomic-weight determinations these films of water must be taken into account as sources of error,[4] as must also the adsorption of the vapour upon the walls of the vessel in exact measurements of vapour density.[5]

The peculiar difference in behaviour of vapour at wettable and non-wettable surfaces is frequently significant. Thus in the daguerreotype the reproduction of the picture depends upon the fact that mercury vapour at saturation pressure condenses upon the exposed silver iodide plate but not upon the unexposed. While silver iodide is a substance which is difficultly wetted by mercury, so that for condensation we have an a, p curve like 2, Fig. 31, light produces a more easily wetted substance—colloidally disperse silver (cf. p. 803)—upon which, in accordance with curve 1, Fig. 31, mercury vapour condenses at saturation pressure.[6] It is naturally not essential that the difference should be so great as between difficultly and easily wetted surfaces; comparatively small differences may be detected, since the eye can plainly distinguish small differences in the shape and the contact angle of deposited drops. In this way a change in the surface of a glass plate under the influence of light can be detected by the illuminated portion appearing as a breath-figure.[7]

[1] Zeitschr. f. physik. Chemie, **91,** 103 (1916).

[2] *Orme Masson* and *E. S. Richards, loc. cit.* p. 163.

[3] Wied. Ann. **27,** 481 (1886); further *Ihmori, ibid.* **31,** 1006 (1887); see also *Cohnstaedt,* Physik. Zeitschr. **10,** 643 (1909).

[4] *Guye* and *Moles,* J. d. Chim. phys. **15,** 360, 405 (1917).

[5] *Drucker* and *Ullmann,* Zeitschr. f. physik. Chemie, **74,** 567 (1910).

[6] Cd vapour acts like Hg vapour [*Kalähne* and *Federlin,* Ber. d. deutsch. physik. Ges. **16,** 931 (1914)].

[7] See the experiments of *Waterhouse* in *Eders'* Photochemie, Vol .I, pp. 116–118, Halle, 1906; *Eders'* Jahrb. f. Phot. p. 599 (1901).

The Heat of Wetting

By the heat of wetting we mean the amount of heat which is developed in the wetting of a solid surface by a liquid. It is none other than the heat of adsorption of vapours at their saturation pressure. It has frequently been determined,[1] although, as an integral heat of adsorption, it is not a very sharply defined physical magnitude (cf. p. 135). Detailed series of measurements by Gaudechon [2] with various adsorbents and liquids supplied the data for the following table. The powders were dried at 100°, the measurement were made at 12–13°.

Table 53

Heat of Wetting in Gram-calories for 1 gram of Adsorbent. t = 12–13°

Liquid.	Heat of Wetting for		
	Clay.	Quartz.	Sugar Charcoal.
Water	12·6	15·3	3·9
Methyl alcohol	11·0	15·3	11·5
Ethyl alcohol	10·8	14·7	6·9
Propyl alcohol	10·2	13·5	5·6
Amyl alcohol	10·1	13·5	3·7
Benzyl alcohol	9·3	13·5	3·7
Formic acid	12	14·5	about 12
Acetic acid	9·3	13·5	6
Butyric acid	7·8	13·5	6
Acetone	8	13·5	3·6
Chloroform	9	8	2·3
Ethyl ether	5·8	8·4	1·2
Benzene	5·8	8·1	4·2
Carbon tetrachloride	1·8	8·1	1·5
Carbon disulphide	1·7	3·6	4
Hydrocarbon (C_5H_{12}, C_6H_{14})	1·2	3·1	0·4

The experiments support the view that the heat of wetting is the greater, the more strongly the liquid is associated. Although we have no guarantee that the various absorbents have the same specific surface, it appears to follow from these values that there is a difference between hydrophobic and hydrophilic adsorbents. In the case of the hydrophobic charcoal, we have a comparatively small heat of wetting for water, a larger one for organic liquids ; in the case of the hydrophilic quartz powder and clay a greater one for water. We are not expressly told, however, whether the charcoal was perfectly wettable.

Parks [3] has shown by special experiments that the heat of wetting is proportional to the area of the boundary surface.

The dependence of the heat of wetting upon temperature in the case of water is remarkable. According to experiments by Schwalbe,[4] confirming

[1] Bibliography in *Schwalbe* [Ann. d. Phys. (4) **16,** 32 (1905)], to which must be added *Melsens* [Ann. de chim. et de phys. (5), **3,** 522 (1874)], *Chappuis* [Wied. Ann. **19,** 21 (1883)] and *Orme Masson* [Proc. Roy. Soc. **74,** 230 (1905)].

[2] Comp. rend. **157,** 209 (1913).

[3] Phil. Mag. (6) **4,** 240 (1902).

[4] *loc. cit.* under [1].

the earlier experiments of Junck,[1] the heat of wetting of various adsorbents by water is positive above 4°, and negative below 4°. As solids silicic acid and various kinds of sand were used, and the temperature changes were measured with a thermo-element. The experiments support the view that in adsorption we are chiefly concerned with the compression in the surface-layer, as far as the qualitative side of the matter goes, a result to which we are of course also led by the unmistakable connection between the adsorbability and condensability of gases. For since water below 4° decreases in volume with rise of temperature, it must, according to a well-known principle of thermodynamics, cool itself upon compression, while above 4°, with a positive coefficient of expansion, the reverse is true.

A further consequence, not yet experimentally tested, of these experiments would be that the temperature coefficient of adsorption of water vapour not far from saturation-point should be positive below 4°, and negative above this temperature.

Upon the heat of wetting depends the phenomenon [2] that, if the bulb of a thermometer is wrapped round with dry flannel and placed in the mouth, the temperature may rise far above the body temperature to about 44°.

General Remarks on the Adsorption of Dissolved Substances

The adsorption of dissolved substances by charcoal and other solids with large surfaces has long been known. A general account of the older literature is to be found in Ostwald's Lehrbuch.[3] This adsorption largely resembles that of gases, and to this extent what was said on p. 106 holds true. At first the discussion will be mainly restricted to solutions of non-dissociated substances, or of substances such as the fatty acids which are only weakly dissociated. Strongly dissociated substances such as salts will be dealt with later. The adsorbents are again mostly solid foams, that is, colloidally disperse structures with a strongly developed inner surface. It is therefore unavoidable that phenomena will now be touched upon, which really belong to the sphere of actual colloid chemistry.

Here again, we can, as for the other boundary surfaces, deduce the Gibbs adsorption formula:

$$\mathfrak{a} = -\frac{c}{RT}\frac{d\sigma_{sf}}{dc}.$$

In putting this to the test, the same considerations apply as in the adsorption of gases; the adsorption is easy to measure, and hence numerous series of measurements are available, from which $\mathfrak{a}$, or a proportional quantity, may be deduced. On the other hand, the dependence of σ_{sf} upon the concentration of the solution has not been determined, because suitable methods of measurement are wanting; hence we have no data for the value of $\frac{d\sigma_{sf}}{dc}$

The Velocity of Adsorption in Solution

The velocity of adsorption in solutions is also entirely in accordance with the theory of surface condensation, such as has proved to be correct for other boundary surfaces (cf. p. 125). The simpler the conditions chosen, and

[1] Pogg. Ann. **125,** 292 (1865).
[2] *Roberts,* Nature, **23,** 55 (1880).
[3] 2nd Edition (1890), Vol. I, p. 1093.

the smaller the difficultly accessible inner surface, the quicker is the adsorption. We again have a strong depletion in a layer directly adjoining the surface-layer, and a diffusion into it from more distant parts of the solution. In the case of well-powdered adsorbents, the equilibrium is mostly reached in seconds or minutes.

Quantitative measurements by Marc and Arendt [1] do not quite correspond to our assumptions. They were carried out with colloidal solutions of starch, albumin, and gum arabic, which are, however, comparatively near to true solutions; strontium carbonate was chiefly used as adsorbent; only a few experiments were carried out with barium carbonate and charcoal. But these experiments may very well be taken as examples, for if with the large slowly diffusing molecules of these sols the adsorption equilibrium was quickly reached, this will certainly be the case for the quickly diffusing molecules of true solutions.

In these measurements the adsorbent, which was at first placed in a thin-walled glass vessel, was released by breaking the latter with a stirrer, and was thus distributed very rapidly in the solution. For the analysis, samples of the liquid could be forced out by pressure from the vessel or removed by a pipette. The rate of adsorption increased with increasing velocity of stirring and was simply proportional to it. At the highest speed of stirring of 190 revolutions a minute, the equilibrium of starch upon strontium carbonate was reached in about 5 seconds, at lower velocities curves were obtained as for the velocity of adsorption in gases (cf. p. 108); 80 to 90 per cent. of the adsorbed material was taken up quickly, in 2 to 3 seconds, the rest more slowly, giving an initially steep x, t curve with a sharp bend. In the case of the adsorption of starch on charcoal, equilibrium was reached in about 2 minutes with a speed of stirring of 600 revolutions per minute. The course of the x, t curve is explained as follows. At first the concentration in the impoverished region is practically zero, the gradient of concentration steep, but shortly before equilibrium is reached it becomes continually flatter. The three constants of the formula proposed by Marc cannot yet be physically interpreted.

In agreement with this diffusion theory we have the further fact, that the initial velocity of adsorption is proportional to the concentration in the solution, and the temperature coefficient is small, about 1·1 for 10°.

The numerous described cases of slow adjustment of adsorption equilibrium may be explained in a natural manner. Either we are really dealing with an adsorption, but the adsorbent possesses so large an inner surface, which is only accessible through fine pores, that the diffusion through these pores can only take place slowly; or we have, instead of pure adsorption, a sorption, and therewith a diffusion of the adsorbed substance into the interior of the adsorbent, that is, a distribution of the former among the molecules of the latter, or a chemical reaction, as the case may be. We may also be dealing with a combination of these cases. And it is difficult, and perhaps arbitrary, to differentiate between an adsorption at an inner surface and a solid solution.

As an adsorption velocity, which is greatly retarded by the structure of the adsorbent, we shall regard the experiments of Lagergren,[2] Siegrist,[3]

[1] *Marc*, Zeitschr. f. Elektrochemie, **20**, 515 (1914); *Arendt*, Kolloidchem., Beihefte **7**, 212 (1915).

[2] Bihg. t. K. Svenska Ak. Hand. **24**, 2, No. 4 and 5 (1899). Velocity of adsorption of succinic acid by animal charcoal.

[3] "Contribution à l'étude des phénomènes d'absorption." Diss., Lausanne, 1910, pp. 15–16. (Velocity of adsorption of dye-stuffs on charcoal and wool.)

Dreyer and Douglas,[1] and others.[2] Cocoanut charcoal is distinguished by a dense structure. This is evident upon wetting, when fine air bubbles escape for many minutes from a small grain; accordingly, the adsorption equilibrium with succinic acid, iodine, and dye-stuffs takes several hours to establish itself, whereas with other wood and animal charcoals only minutes are necessary.[3] Since under these conditions the uniformly strong depletion of the layer in front of the adsorption layer is much longer maintained, the velocity can be calculated over a fair length of time, as a diffusion velocity with constant gradient of concentration, by means of a reaction equation of the first order (for instance, the experiments of Lagergren).

The kinetics in the case of a sorption are similar, only that here the adsorption proceeds quickly at the interface, and the diffusion into the interior occurs slowly, at a practically constant gradient of concentration. Experiments, where we might certainly reckon with solid solution combined with adsorption, are those of McBain[4] on the taking up of iodine by charcoal in organic solvents such as toluene. Over a period of more than 11 years a continuous diminution in the iodine concentration was observed, and yet initially the end states are reached reversibly within 24 hours. For these the ordinary isothermal is to a great extent valid, while the dependence upon the concentration changes in course of time, no doubt on account of the formation of a solid solution. That thereby no chemical reaction takes place to an appreciable degree was specially proved. v. Georgievics and Dietl[5] consider—probably correctly—the taking-up of acids by wool as a sorption and find a parallelism with the coefficient of diffusion and a comparatively small temperature coefficient of 1·5 at 10°.

They found, in agreement with earlier observations by W. Ostwald,[6] that the adsorption equilibrium is set up more quickly when adsorption is allowed to take place from a concentrated solution which is subsequently diluted, than when the equilibrium is set up directly from a dilute solution. This can be explained as follows: according to the adsorption isothermal, which also holds for adsorption in solution (cf p. 172), the amount adsorbed changes comparatively little with the concentration of the solution. If therefore this is diluted, only a fairly small amount of the adsorbed material need return to the solution. The interface, which stands in free exchange with the solution, is large enough to give up this amount quickly, as in McBain's experiments with gases (cf. p. 109). The exchange in the interior of the adsorbent is concerned with such small amounts that they hardly influence in course of time the concentration of the solution. That the attainment of equilibrium upon the adsorbent first being brought into contact with the solution takes a longer time only depends upon the fact that the inner surface of the adsorbent then carries absolutely no adsorbed material; this total amount is of course sufficiently large for the longer time required for the attainment of equilibrium to make itself felt. If we have only an easily accessible inner surface and no sorption, this difference naturally disappears.

[1] Proc. Roy. Soc. **82,** B, 168 (1910). Velocity of adsorption of agglutinin by bacteria and charcoal, trypsin by charcoal, etc.

[2] See also *G. C. Schmidt,* Zeitschr. f. physik. Chemie, **74,** 704 *et seq.* (1910); **77,** 646 *et seq.* (1911).

[3] Unpublished experiments of *H. Fischer.*

[4] Trans. Faraday Soc. **14,** part 3 (1919).

[5] Zeitschr. f. physik. Chemie, **87,** 669 (1914); Wien. Monatshefte, **35,** 643 (1914); *Dietl,* Kolloidchem., Beihefte **6,** 127 (1914); Wien. Monatshefte, **35,** 795 (1914).

[6] Lehrb., 2nd Ed. Vol. I, pp. 1097–1098.

The Adsorption Isothermal in Dilute Solutions

As in the adsorption of gases, so also in adsorption from dilute solutions, the ordinary adsorption isothermal

$$a = ac^{\frac{1}{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is generally valid. Here c is the equilibrium concentration in the solution after adsorption. The remaining quantities have the meaning given on p. 111. Aqueous solutions of non- or weakly dissociated, and even of strongly dissociated, substances, solutions in benzene, alcohols, ether, and concentrated sulphuric acid, have been investigated, using the most diverse adsorbents (carbon, wool, silk, kieselguhr, arsenic trisulphide, and many others), and in practically every case the above-mentioned equation has been shown to hold.[1] It may be applied under certain circumstances even to extremely dilute solutions. Trümpler[2] showed that the adsorption

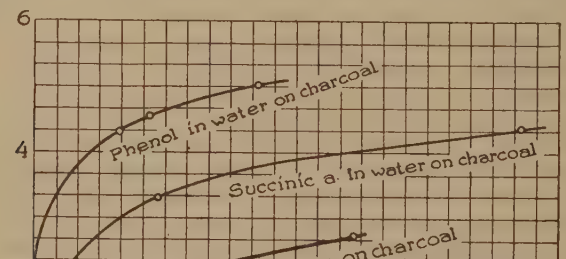


Fig. 33A.—Adsorption Isothermals of Solutions.

of fluorescein in alkaline aqueous solution by animal charcoal may be represented by this equation down to a concentration of 0·000001 gram (= 0·003 micromols per litre). In Figs. 33A and B, the a, c curves in the former case and the $\log_{10}a$, $\log_{10}c$ curves in the latter are plotted for a number of solutions, c in mol per litre, a in millimol per gram. That the curves on the logarithmic diagram are practically straight lines is a proof that the isothermal holds. It should be noted that a always denotes the amount adsorbed referred to unit quantity of adsorbent. The following tables, which, except for Tables 54 and 55, are taken from my own experiments, and in which the a values calculated from the equation are set alongside those found experimentally, are further evidence for the existence of the law. The concentration c is in mol per litre, the amount adsorbed in millimol per gram of carbon.

[1] See especially *G. C. Schmidt*, Zeitschr. f. physik. Chemie, **15**, 56 (1894); *v. Georgievics*, Wien. Monatshefte, **15**, 705 (1894); *Appleyard* and *Walker*, Journ. Chem. Soc. **69**, 1334 (1896); *Freundlich*, Zeitschr. f. physik. Chemie, **57**, 385 (1907); **73**, 385 (1910).

[2] Kolloidzeitschr. **15**, 10 (1914).

TABLE 54 [1]

Adsorption of Acetone in Water on Blood-charcoal

$a = 5.12$; $\frac{1}{n} = 0.52$; $t = 18°$

c.	a (obs.).	a (calc.).
0·00234	0·208	0·219
0·01465	0·618	0·569
0·04103	1·075	1·03
0·08862	1·50	1·45
0·17759	2·08	2·08
0·26897	2·88	2·59

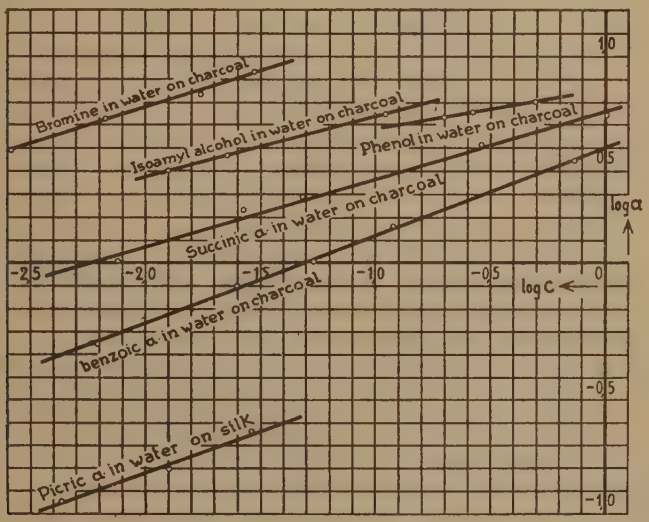


FIG. 33B.—Adsorption Isothermals for Solutions plotted logarithmically.

TABLE 55 [2]

Adsorption of Isoamyl Alcohol in Water on Blood-charcoal

$a = 7·93$; $\frac{1}{n} = 0·263$; $t = 15°$

c.	a (obs.).	a (calc.).
0·0125	2·52	2·51
0·0225	2·95	2·92
0·1100	4·45	4·44

[1] *L. Michaelis* and *Rona*, Biochem. Zeitschr. **15**, 196 (1908).
[2] *van Duin*, Kolloidzeitschr. **17**, 129 (1915).

TABLE 56

Adsorption of Bromine in Water on Blood-charcoal

$$a = 23{\cdot}12\,;\ \frac{1}{n} = 0{\cdot}340\,;\ t = 0°$$

c.	a (obs.).	a (calc.).
0·00092	2·07	2·19
0·00259	3·10	3·01
0·00669	4·27	4·15
0·01708	5·44	5·73
0·02975	6·80	6·87

TABLE 57

Adsorption of Benzoic Acid in Benzene on Blood-charcoal

$$a = 3{\cdot}243\,;\ \frac{1}{n} = 0{\cdot}396\,;\ t = 25°$$

c.	a (obs.).	a (calc.).
0·00618	0·437	0·445
0·02500	0·780	0·767
0·05313	1·04	1·04
0·1177	1·44	1·41

Adsorption experiments in solution are easy to carry out; the weighed amount of the adsorbent is shaken with a measured volume of a solution of known concentration, the adsorbent is removed, either by decantation or centrifuging, and the concentration of the solution is re-determined. The quantity of adsorbent and the volume of the solution are conveniently chosen so that as far as possible a decrease in concentration of 30 to 60 per cent. takes place. The temperature effect is usually so small that one can dispense with a thermostat.

That here also well-defined equilibria are set up is naturally assumed in the foregoing consideration of the matter. This assumption is strictly confirmed by experiment. In Table 58 are given some experiments, in which in one case the solution was added directly to the adsorbent, in another case half the volume of solution was taken of double strength and brought into equilibrium with the same amount of adsorbent, and then diluted with a second half-volume of solvent. If we have equilibria which are accurately set up, the final concentrations should be the same in the two cases, which is indeed true.

The adsorption exponent $\frac{1}{n}$ lies in general between 0·1 and 0·5 (see Table 59). It is therefore as a rule smaller than in the case of gas adsorption.

Another peculiar regularity is to be mentioned,[1] which is not comprised in formula (1). It has, as we shall see, certain theoretical objections, but often proves convenient for practical measurement, and contains formula (1) as a special case.

[1] See *Freundlich, loc. cit.* p. 172. Further confirmation of this regularity in *Aberson*, Kolloidzeitschr. **10**, 13 (1912); *Gustafson*, Zeitschr. f. physik. Chemie, **91**, 397 (1916).

TABLE 58

Attainment of Equilibrium in Adsorption from Solution

Solvent and Solute.	$c\left(\frac{\text{mol}}{\text{litre}}\right)$	Observations.
Acetic acid in water (t = 25°) .	0·06078	1 gram blood-charcoal with 100 c.c. of a 0·0688 molar solution, shaken 20·5 hours.
„ „ „ „ .	0·06064	1 gram blood-charcoal shaken 21 hours with 50 c.c. of a 0·1376 molar solution, then 50 c.c. water added, and shaken 3 hours.
Benzoic acid in benzene (t = 25°)	0·1177	1 gram blood-charcoal shaken with 100 c.c. of a 0·1321 molar solution.
„ „ „ „	0·1179	1 gram blood-charcoal shaken with 50 c.c. of a 0·2642 molar solution; after 2 hours 50 c.c. benzene added and again shaken.

TABLE 59

Values of the Adsorption Exponent $\frac{1}{n}$

Adsorbent.	Solvent.	Substance adsorbed.	$\frac{1}{n}$	Observer.
Blood-charcoal	Water . .	Formic acid . . .	0·451	Freundlich [1]
„ „	„ . .	Acetic acid . . .	0·425	„
„ „	„ . .	Propionic acid . .	0·394	„
„ „	„ . .	Butyric acid . .	0·301	„
„ „	„ . .	Monochloroacetic acid	0·363	„
„ „	„ . .	Succinic acid . .	0·243	„
„ „	„ . .	Benzoic acid. . .	0·338	„
„ „	„ . .	Picric acid . . .	0·240	„
„ „	„ . .	Chlorine	0·297	„
„ „	„ . .	Bromine	0·340	„
„ „	„ . .	Phenylthiourea . .	0·245	Freundlich & Bjercke [2]
„ „	„ . .	Acetone	0·52	L. Michaelis & Rona [3]
„ „	„ . .	Glucose	0·474	R. O. Herzog [4]
„ „	„ . .	Fructose	0·539	„
„ „	„ . .	Isobutyl alcohol. .	0·555	van Duin [5]
„ „	„ . .	Isoamyl alcohol . .	0·263	„
„ „	Benzene .	Acetic acid . . .	0·419	Freundlich [1]
„ „	„ .	Benzoic acid. . .	0·416	„
„ „	Ethyl ether	„ „ . . .	0·455	„
„ „	„ „	Bromine	0·263	„
„ „	Conc. H_2SO_4	„	0·351	„
Animal „	Alcohol .	Iodine	0·324	Davis [6]
„ „	Chloroform	„	0·336	„
„ „	Benzene .	„	0·311	„
Silk . . .	Water . .	Picric acid . . .	0·347	Appleyard & Walker [7]
„ . . .	Alcohol .	„ „ . . .	0·363	„ „

[1] *loc. cit.* p. 172. [2] Zeitschr. f. physik. Chemie, **91**, 1 (1916).
[3] Biochem. Zeitschr. **15**, 196 (1908).
[4] Zeitschr. f. physiol. Chemie, **60**, 79 (1909); see on the adsorption of sugar also *Rona* and *Michaelis*, Biochem. Zeitschr. **16**, 489 (1909).
[5] Kolloidzeitschr. **17**, 123 (1915).
[6] Journ. Chem. Soc. **91**, 1666 (1907). [7] *loc. cit.* p. 172.

If we add to a given initial solution, in which y mols of a substance are dissolved in volume v, varying amounts m of the adsorbent, we get various equilibrium concentrations c. When y is given, c obviously depends upon the ratio of the quantities of the two phases v and m. If we plot for a given y the c, m curve, we get a logarithmic curve ; c declines logarithmically with increase in m, the adsorbed amounts increase logarithmically. The differential equation

$$dx = \lambda \frac{y - x}{v} dm \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

holds, in which λ is a constant. On integration

$$\lambda = \frac{v}{m} \log \frac{y}{y - x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The extent to which this regularity holds good is shown by Tables 60 and 61, in which in one case only m, in the other m and v are varied.

TABLE 60

λ-Values for the Adsorption of Acetic Acid in Water on Blood-charcoal
$t = 25°$

$y = 6{\cdot}5175$ Millimol contained in $v = 50$ c.c.

m (in Grams).	$y - x$ (in Millimols).	λ.
0·187	6·3084	8·71
0·338	6·1267	9·15
0·765	5·6539	9·29
1·234	5·2100	9·06
1·957	4·5780	9·02
3·445	3·5946	8·63

TABLE 61

λ-Values for the Adsorption of Acetic Acid in Water on Blood-charcoal
$t = 25°$

m (in Grams).	v (in c.c.).	in which y	or $y - x$ Millimols resp. were contained.	λ.
0·689	50	10·458	9·553	6·57
1·577	100	20·916	18·812	6·72
1·647	150	31·374	29·101	6·85
3·020	200	41·832	37·830	6·66

The differential equation (2) is the simplest imaginable, if a substance distributes itself between two phases ; the amount dx of the dissolved substance entering the second phase, the adsorption layer, upon its being increased is proportional to the concentration in the solution $\frac{y - x}{v}$. If we inquire under what conditions, say as compared with the distribution according to Henry's law, a differential equation of this kind would appear, we arrive at the following result. If we differentiate the equation which would hold according to Henry's law

$$\frac{\frac{x}{m}}{\frac{y - x}{v}} = \lambda$$

we get

$$dx = \lambda \frac{y-x}{v} \cdot \frac{v}{v+\lambda m} dm \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The difference between formulæ (2) and (4) consists in the fact that in (4) the volume of both phases takes effect in the same sense, an expression of the fact that van 't Hoff's laws hold in both phases. In the case of adsorption, this is not so, under the conditions for which equation (2) is valid. The volume of the adsorption layer does not enter into action with the same function as that of the solution. The adsorbed substance passes into a state in which the volume which it occupies does not—within certain limits—play a part.[1]

If formula (2) becomes so far comprehensible, the following still remains to be explained. According to equations (2) and (3) we can represent the relation between the amount adsorbed $a = \frac{x}{m}$ and the concentration in the solution $c = \frac{y-x}{v}$ by a single constant λ, whereas the adsorption isothermal requires two. This contradiction, which was pointed out by *McBain*,[2] was explained by *Masius*.[3] If we form from equation (3) the differential coefficient

$$\frac{d \log a}{d \log c} = \frac{d \log \frac{x}{m}}{d \log \frac{y-x}{v}} = \frac{\frac{x}{y} - \left(1 - \frac{x}{y}\right) \log \frac{1}{1-\frac{x}{y}}}{\frac{x}{y} \log \frac{1}{1-\frac{x}{y}}},$$

then it should, according to the adsorption isothermal, be constant and equal to $\frac{1}{n}$. It is not. On the contrary, it is dependent upon the ratio $\frac{x}{y}$. But it proves to be practically constant, and equal to 0·48 over a range of values of $\frac{x}{y}$ from 0·05 to 0·50. It is because $\frac{1}{n}$ is generally only slightly different from 0·5, and because the experiments are usually performed in such a way that about 50 per cent. of the solute is adsorbed, that formula (3) is so generally fulfilled.

If we take various initial concentrations y, we actually get different values of λ, which are connected with y by an equation

$$\lambda = \frac{v}{m} \log \frac{y}{y-x} = \beta \left(\frac{y}{v}\right)^{-\frac{1}{p}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

How far it holds is shown by the following table:

TABLE 62

Adsorption of Acetic Acid on Blood-charcoal

$$\beta = 2{\cdot}999\,; \quad \frac{1}{p} = 0{\cdot}526\,; \quad t = 25°$$

$\frac{y}{v}$ Mol/Litre.	λ (obs.).	λ (calc.).
0·02622	20·8	21·0
0·04705	16·2	15·4
0·08078	11·5	11·5
0·15040	8·30	8·30
0·30209	5·54	5·65
0·52419	4·11	4·24

[1] We may not neglect λm as compared with v. For even if the true surface volume v_ω, in which the adsorbed substance is contained, and which is proportional to m, is very small, we should have to take a correspondingly larger λ into account, if we reckoned with v_ω instead of m.

[2] Journ. Chem. Soc. **91**, 1683 (1907).

[3] "Über die Adsorption in Gemischen." Diss., Leipzig, 1908, p. 48 *et seq.*

$\frac{1}{p}$ is now the second constant. How it is connected with the $\frac{1}{n}$ of the adsorption isothermal, and that equation (5) can actually pass over into the latter, becomes clear when we develop formula (5) in series on both sides. We find

$$\frac{x}{m} = \beta\left(\frac{y-x}{v}\right)^{1-\frac{1}{p}} \cdot \frac{1 + \left(1 - \frac{1}{p}\right)\frac{x}{y} \cdots}{1 + \frac{1}{2}\frac{x}{y} \cdots}.$$

If we neglect the higher terms, and remember that $\frac{y-x}{v} = c$, then we get the ordinary adsorption isothermal

$$\frac{x}{m} = a = \beta c^{1-\frac{1}{p}}.$$

Hence $\beta = a$ and $1 - \frac{1}{p} = \frac{1}{n}$. In the case of the λ formula therefore we put the adsorption isothermal as it were together piecemeal with the help of distribution coefficients λ, which can only be applied within a certain range of concentration, and only when $\frac{1}{n}$ is not too different from 0·5.

In spite of these objections against the λ formula, it has advantages in so far as it allows of a simple pre-calculation of the equilibrium concentration and adsorbed amount in the case of a solution of given initial concentration and with known quantity of adsorbent and known volume.

A less general, but otherwise useful way to solve the problem of calculating the equilibrium concentration from the initial concentration has been given by Mecklenburg.[1] The sum of x, the amount adsorbed, and $y - x$, the amount in solution at equilibrium, is always equal to the initial amount y. If the adsorption isothermal for constant volume and constant amount of adsorbent be plotted with x and $y - x$ as co-ordinates, and y be then marked off upon the two axes of co-ordinates, the hypotenuse of the isosceles right-angled triangle formed by joining these two points cuts the isothermal in a point (shown in Fig. 34), which fulfils the conditions for adsorption and the abscissa of which gives the amount of solute present in the solution when in equilibrium.

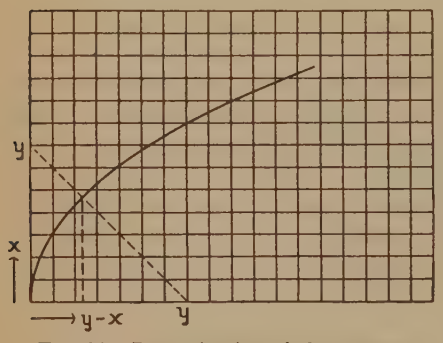


Fig. 34.—Determination of the amount Adsorbed from the Initial Concentration.

With the help of the λ formula, a certain case of adsorption can be conveniently deduced, to which Lockemann [2] and his co-workers have paid attention. They measured in the case of the adsorption of arsenious acid by iron hydroxide, the *total adsorption*, that is, they determined the amount of adsorbent m_T which was just required to adsorb the dissolved substance completely from a constant volume of solution. The equation thereby observed,

$$m_T = Kx^{\frac{1}{p}} \quad \cdots \quad (6)$$

[1] Naturwiss. Wochenschrift, **15**, 409 (1916).

[2] *Lockemann* and *Paucke*, Kolloidzeitschr. **8**, 273 (1911); *Lockemann* and *Lucius*, Zeitschr. f. physik. Chemie, **83**, 735 (1913).

may be deduced in the following manner from the λ formula. Let x always be the same, very large, fraction of y (which will be approximately correct). Then, according to equation (3), since $\log \frac{y}{y-x}$ and v are constant, m_T is proportional to the reciprocal value of λ. Hence

$$m_T = \frac{\text{Const.}}{\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If we write equation (5) in the form

$$\frac{1}{\lambda} = \frac{1}{\beta}\left(\frac{y}{v}\right)^{\frac{1}{p}}$$

it then passes into equation (6), if we substitute from formula (7), neglect the difference between the adsorbed amount x and the initial amount, keep v constant and collect the constants to a single one.

Adsorption in Concentrated Solutions

Adsorption in concentrated solution requires, as A. M. Williams [1] in particular has emphasized, another mode of examination; certain circumstances must be taken into account which may be safely neglected in dilute solution. In the first place, the volume of the solution after adsorption may not be put equal to the initial volume without further question. And then, strictly speaking, we must always reckon with the possibility of the solvent being adsorbed, and the more we approach in the case of concentrated solutions the region in which the solvent is present in lesser amount than the solute, and may be itself regarded as solute, the more this point requires consideration.

We will now consider a complete adsorption curve, beginning therefore with the adsorption of substance B from solvent A, and continuing to the adsorption of A from solvent B. With Williams we will refer everything to weight and not to volume. Let γ_0 grams of the solute B be contained in 1 gram of the solution before adsorption and γ grams after adsorption. If we have G grams of the solution, and assume for the present that the solvent is not also adsorbed, then the amount of substance adsorbed is

$$X' = G\gamma_0 - G\frac{1-\gamma_0}{1-\gamma}\gamma = G\frac{\gamma_0 - \gamma}{1-\gamma} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$G\frac{1-\gamma_0}{1-\gamma}$ is obviously the weight of the solution after adsorption, if the solvent is not adsorbed. In the case of dilute solutions γ can be neglected as compared with 1, and the amount adsorbed is, as has always otherwise been calculated, $G(\gamma_0 - \gamma)$.

Now let Y grams of the solvent A be adsorbed. The *apparent adsorption* X′ of the dissolved substance is then smaller than the *true adsorption* X, since on account of the adsorption of the solvent, the solution after adsorption is correspondingly more concentrated, and X′, calculated from equation (1), will turn out smaller. The difference between X and X′ obviously corresponds to the quantity of solute which was associated with amount Y of solvent in the solution. This amounts to $Y\frac{\gamma}{1-\gamma}$. We therefore have

[1] Medd. fr. K. Vet. Ak. d. Nobelinst. (2), Nr. 27 (1913).

the equation

$$X - X' = Y\frac{\gamma}{1-\gamma}$$

or

$$X' = X - Y\frac{\gamma}{1-\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

X and Y in these equations are unknown to us, whereas we can always calculate the apparent adsorption X′ from equation (1).

X and Y are also always positive, while X′ can be both positive and negative. Accordingly we speak of a *positive adsorption* when $X > Y\frac{\gamma}{1-\gamma}$ or $\frac{X}{Y} > \frac{\gamma}{1-\gamma}$, and of a *negative adsorption* when $X < Y\frac{\gamma}{1-\gamma}$ or $\frac{X}{Y} < \frac{\gamma}{1-\gamma}$. We have an apparent adsorption 0 when solvent and solute are adsorbed in the ratio in which they were originally present in the solution, when therefore $\gamma_0 = \gamma$ and $\frac{X}{Y} = \frac{\gamma}{1-\gamma}$. We see that a positive adsorption of B corresponds to a negative adsorption of the solvent A, and a negative of B to a positive of A.

In order to get an insight into the probable course of the dependence of X′ upon γ, we may start from the probable form of the interfacial tension—concentration curve, as represented in Fig. 11. If we assume that the σ, c curve has a minimum, then the substance B lowers the interfacial tension of A as does A that of B. Hence there will be positive adsorption both of B in A and of A in B. As we are only considering the adsorption of B in A, positive adsorption of A in B means negative of B in A in the range of concentration not far removed from the pure solvent B. We have therefore on the A side at first a rise in the amount adsorbed according to the usual rise in the adsorption isothermal, on the B side a negative adsorption which becomes the greater the more we approach B—this on account of the fact that in equation (1) the denominator decreases continuously with increase of concentration, and not on account of an increase or of appreciably large negative values of $(\gamma_0 - \gamma)$. The two branches of the curve when joined give a diagram such as is shown in Fig. 35; the adsorption curve reaches a maximum and cuts the axis of abscissæ at a certain distance from B. This point signifies an adsorption 0 corresponding to the case above-mentioned, that solvent and solute are adsorbed in the same proportion as that in which they are present in the solution. The end-point of the curve on the B side must be left indeterminate, since in actual adsorption experiments of the kind discussed here it is impossible to determine the adsorption of the pure solvent itself.[1] In Fig. 35 the concentra-

[1] We might be tempted to regard the minimum in the σ, c curve as the point in which, since $\frac{d\sigma}{dc} = 0$, the adsorbed amount also becomes zero, in accordance with the *Gibbs* adsorption-equation $a = -\frac{c}{RT}\frac{d\sigma}{dc}$; this minimum would then correspond to the point at which the general adsorption curve cuts the axis of abscissæ. This conclusion is not allowable without further question, since the Gibbs equation is deduced (see *Scientific Papers*, Vol. II) expressly upon the assumption that the change of potential of the solvent, and therefore its adsorption, are neglected. The same applies to the assumption which one might incline to make, that the maximum in the general adsorption curve arises from the diminution of $\frac{d\sigma}{dc}$ being compensated in a certain range of concentrations by an increase in c.

tions are plotted in grams of solute in 1 gram of solution as abscissæ, the amounts adsorbed in grams per gram of adsorbent as ordinates.

If the σ, c curve has no minimum, the X', γ curve does not cut the axis; it reaches a maximum, to fall off again towards the B side.

This ought therefore to be the course of the general adsorption curve, also for concentrated solutions. Williams could not realize it for the adsorption of acetic acid in water by blood-charcoal; in the range of possible measurement it was still on the ascending part, although it appeared probable that at quite high concentrations a negative adsorption of the acetic acid takes place. Frau Schmidt-Walter [1] also obtained with aqueous acetic acid solutions and animal charcoal only an ascending curve; but with the same adsorbent and solutions of acetic acid in benzene and toluene she observed a maximum and a subsequent decline to a very considerable negative adsorption. Curve 1 in Fig. 35 is the adsorption of acetic acid in toluene as measured by her, which follows entirely the course just discussed theoretically. Table 63 contains the corresponding figures.

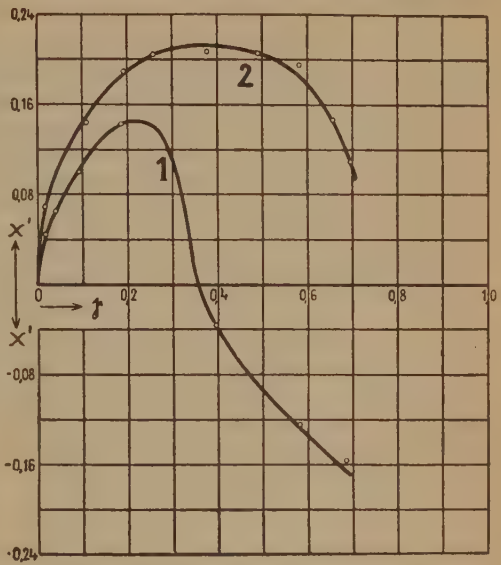


Fig. 35.—General Adsorption Isothermals of Solutions.

Table 63 [2]

Adsorption of Acetic Acid in Toluene on Animal Charcoal up to High Concentrations. Room Temp.

γ (gram Acetic Acid to 1 gram Solution).	X′ (gram Acetic Acid to 1 gram Carbon).
0·00084	+ 0·0133
0·00309	+ 0·0206
0·00648	+ 0·0302
0·01546	+ 0·0446
0·03680	+ 0·0644
0·09090	+ 0·0990
0·1808	+ 0·132
0·3962	— 0·0373
0·5802	— 0·124
0·6838	— 0·157
0·8538	— 0·433

[1] Kolloidzeitschr. **14**, 242 (1914).

[2] According to experiments by Frau *Schmidt-Walter* [Kolloidzeitschr. **14**, 251 (1914)], the values have been multiplied by $\frac{1}{1-\gamma}$ in order to take into account the change in volume after adsorption.

A further example is found in curve 2 of Fig. 35; it relates to the adsorption of phenol in ethyl alcohol upon animal charcoal according to experiments by Gustafson.[1] Here likewise a negative adsorption should obviously occur at still higher concentrations; it could not be determined, since at these high phenol concentrations the carbon remained colloidally suspended.

A large number of other experimental results agree with this general adsorption curve. The rather flat maximum of adsorption frequently extends over a considerable range of concentration. G. C. Schmidt[2] emphasized the occurrence of this maximum value and described it as a *saturation*, which the amount adsorbed approaches with increasing concentration. Schmidt, however, calculated the amount adsorbed in exactly the same manner as for dilute solutions (cf. p. 179); but even when the calculation is correctly carried out a saturation of this kind is frequently reached (see curve 2, Fig. 35). The adsorption formulæ put forward by Schmidt[3] and Arrhenius,[4] which introduce a saturation value, without taking into account the adsorption of the solvent, are, according to Williams' view referred to above, incorrect.

At about the same time as Schmidt, Marc[5] drew attention to saturation in connexion with adsorption. He examined, however, adsorbents and solutions which were quite different and, strictly speaking, should not be introduced at this stage; as adsorbents he used crystalline substances such as strontium and barium carbonates, barium sulphate; as solutions, aqueous solutions of hydrophilic colloids such as starch, gum, and the like, or of dyes such as bismarck brown, ponceau, and patent blue. We must therefore be cautious in two directions: on the one hand, in the case of adsorption by crystalline substances, circumstances must be taken into account which are negligible in the case of amorphous substances (see p. 218); further, in the case of hydrophilic colloids we have to reckon with the possibility of coagulation. Moreover the dyes can only in part and under certain conditions be regarded as truly dissolved, and above all, they are strongly dissociated. But it is extremely probable that the saturation observed by Marc corresponds to the saturation in the general adsorption curve. That it is already reached at low concentrations, and not only at high ones, does not by any means contradict this view. In the case of strongly adsorbable substances, the maximum may already occur at small concentrations, just as in the case of strongly surface-active substances the minimum in the σ, c curve is already reached at low concentrations.

One or two results may be mentioned; for instance, a saturation in the adsorption of crystal violet by charcoal and fibres,[6] and also a maximum

[1] *loc. cit.* p. 174.

[2] Zeitschr. f. physik. Chemie, **74**, 689 (1910).

[3] *loc. cit.* under [2]. Further, Zeitschr. f. physik. Chemie, **77**, 641 (1911); **78**, 667 (1912); **83**, 674 (1913); see the criticisms of *Marc*, Zeitschr. f. physik. Chemie, **76**, 58 (1911); **81**, 677 *et seq.* (1913).

[4] Meddel. fr. K. Vet. Akad. Nobelinst. (2), Nr. 7 (1911).

[5] Zeitschr. f. physik. Chemie, **75**, 710 (1911); **81**, 641 (1913).

[6] *Freundlich* and *Losev*, Zeitschr. f. physik. Chemie, **59**, 284 (1907). We get namely for crystal violet in the λ formula [formula (5) p. 177] $\frac{1}{p}$ about equal to 1, and thence in the adsorption isothermal $\frac{1}{n} = 0$; that is, the amount adsorbed is independent of the concentration of the solution.

and subsequent fall with rising concentration in the adsorption of strychnine nitrate by blood-charcoal, bole, and arsenic trisulphide.[1]

The "anomalous adsorption" described by W. Biltz and Steiner[2] relates to dyes such as night blue, and Victoria-blue, which are in great degree to be regarded as hydrophilic colloids. But after what has been said above concerning the experiments of Marc, and in view of the continuous transition from true to hydrophilic colloid solutions (cf. p. 531), it is still quite probable that the anomalous adsorption curves, which the investigators in question obtained for the adsorption of night blue and Victoria blue upon cotton and charcoal, correspond in their sharply defined maximum to the general adsorption curve. It is noteworthy, as pointed out likewise by Biltz and Steiner, that the adsorption of agglutinin by bacteria, according to G. Dreyer and J. S. C. Douglas,[3] also shows a maximum and subsequent decline at high concentrations.

The fact repeatedly mentioned in the literature,[4] that the log a, log c straight lines tend to bend with increasing c toward the log c axis, is only an expression of the fact that the ordinary isothermal is ceasing to hold and the maximum is being approached.

In short, the vast majority of not quite regular adsorption curves show, with increasing concentration, a maximum in the amount adsorbed, and, on occasion, a subsequent decline to a negative adsorption. This is entirely in accordance with the general adsorption curve predicted theoretically. The ordinary adsorption isothermal (see p. 172) may only be applied to dilute solutions, where the meaning of "dilute" may be different from substance to substance, according to the concentration at which the maximum of adsorption is reached.

The observation of H. Morawitz,[5] that when small amounts of adsorbent are used the amount adsorbed is smaller than corresponds to the adsorption isothermals measured with larger quantities, cannot be immediately explained upon these lines. He believes himself justified in concluding that capillary electrical influences are at work, since the settling of the adsorbent (charcoal in aqueous solution of succinic acid) takes place surprisingly slowly. Regarding the unusual isothermal described by Gurwitsch[6] in the case of the adsorption of acids such as benzoic or valeric by fuller's earth in solutions of light petroleum or benzene, it would be advisable to ascertain whether part of the acid is not neutralized by the fuller's earth; the formula given by Gurwitsch would indeed result, if, in addition to adsorption, a neutralization of this kind took place.

What we have hitherto considered was the *apparent* adsorption X′, which alone we are able to measure directly. In order to determine the *true* adsorptions of solute and solvent X and Y, we must have a second independent equation, which contains both quantities individually or together. A. M. Williams[7] tried to obtain such an equation as follows.

[1] *Freundlich*, Zeitschr. f. physik. Chemie, **73**, 400 (1910); *Freundlich* and *Poser*, Kolloidchem. Beihefte **6**, 295 (1914).

[2] Kolloidzeitschr. **7**, 113 (1910). The adsorption of congo-red in alcohol-water solution by filter paper investigated by *Bayliss* [Biochem. Journ. **1**, 178 (1906)] also shows a maximum.

[3] Proc. Roy. Soc. **82**, B, 185 (1910).

[4] e.g. *Freundlich*, Zeitschr. f. physik. Chemie, **57**, 391 (1907).

[5] Kolloidchem. Beihefte **1**, 308 *et seq.* (1910).

[6] Zeitschr. f. physik. Chemie, **87**, 323 (1914).

[7] *loc. cit.* p. 179.

If the adsorbent is allowed to saturate itself in the vapour space above the solution (say acetic acid—water), then the amount thus taken up must be equal, according to the Second Law, to that which would be adsorbed in solution; the increase in weight which the adsorbent shows when equilibrium is reached would therefore be

$$Z = X + Y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Owing, however, to the considerations given on p. 167, the adsorption of vapour at saturation is ill-defined, since equilibrium is set up slowly and imperfectly, and this is particularly the case with such adsorbents as charcoal, which, like all solid foams, have a large inner surface. Nevertheless, the following calculation by Gustafson [1] is worthy of attention. On the basis of Williams's measurements he evaluated, using equations (2) and (3), the true amounts of acetic acid X and water Y adsorbed. He also obtained from these equations the amounts X_∞ Y_∞ adsorbed in the pure liquids or their vapours as the case may be. It now appeared that the true adsorbed amount of acetic acid, even for the high concentrations at which the adsorp-

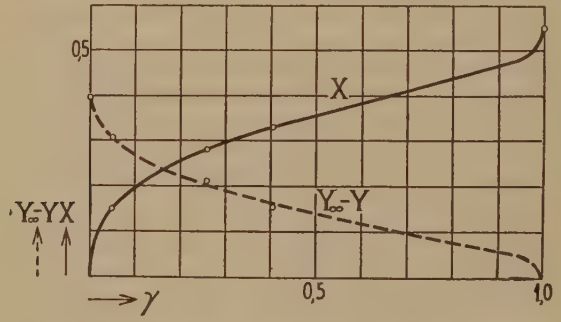


Fig. 36.—Adsorption Isothermals of Solvent and Solute.

tion of the vapours was measured, could be represented by the ordinary adsorption isothermal

$$X = a_X \gamma^{\frac{1}{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Indeed, this equation held good, even with the same constants, for the adsorbed amounts directly determined in dilute solution, where there is no need to distinguish between X and X′; with the values $a_X = 0{\cdot}467$ and $\frac{1}{n} = 0{\cdot}38$ the true adsorption of acetic acid by animal charcoal could therefore be represented over a range of concentration from $\gamma = 0{\cdot}0000325$ to $\gamma = 0{\cdot}4073$. Even more: the decrease in the amount of solvent adsorbed, its displacement, as it were, by the solute, could also be represented by an adsorption isotherm

$$Y_\infty - Y = a_Y \gamma^{\frac{1}{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The figures were $a_Y = 0{\cdot}347$ and $\frac{1}{n} = 0{\cdot}457$. The true adsorption of solute and solvent would therefore be represented, if these considerations should prove to be generally applicable, by two curves as shown in Fig. 36, in which ordinates and abscissæ are on the same scale as in Fig. 35.

[1] Zeitschr. f. physik. Chemie, **91**, 405 *et seq.* (1916).

The Adsorption Isothermal in Solutions from the Point of View of Surface Attraction

Polanyi [1] has also applied his argument discussed on p. 123 to adsorption in solutions; he assumes that the adsorbed substance has a limited solubility. We might at first think that from formula (1), p. 125, it should follow for adsorption in solutions that

$$\varepsilon_A = RT \log \frac{L}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here ε_A is the adsorption potential of the adsorbed substance, L its solubility, c the equilibrium concentration in the solution. If we now attempt to bring ε_A into relation with the adsorption volume φ_A and to represent this again as function of the amount adsorbed, we see that this cannot be done so simply as in the case of gases. For the adsorption volume contains molecules of solvent as well as of adsorbed substance. Even equation (1) no longer holds, for the molecules of the solvent exert, as it were, a pressure upon the adsorbed portion of the solute, and increase its volatility, as it were; just as the pressure of foreign gas molecules increases the vapour pressure of a liquid; or otherwise expressed, the solvent is adsorbed and tends to displace the solute. The work corresponding to the adsorption potential is therefore greater than assumed by equation (1). Polanyi thus reaches the conclusion that for ε_A the equation

$$\varepsilon_A = RT \log \frac{L}{c} + \varepsilon_M \frac{V_A}{V_M} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

really holds. Here ε_M is the adsorption potential of the solvent, V_A and V_M are the molecular volumes of adsorbed substance and solvent.

No other extensive measurements are available, from which the individual adsorption of solvent and solute might be deduced in order to verify equation (2). A few essentially qualitative conclusions will be touched on later (p. 194).

Also the form in which the adsorbed substance may be supposed to exist, especially when it is apt to occur as crystalline solid, will be dealt with later (cf. p. 811).

The adsorption isothermal of Williams (cf. p. 130), which proved of much value for gases, agrees less well than the ordinary isothermal for the adsorption in highly concentrated solutions, while it shows good agreement at small concentrations (under 50 millimol per litre). The fact makes itself felt that we are usually dealing in the case of gases with smaller molar concentrations. The concentration of a gas at atmospheric pressure is only about 40 millimol per litre.

The Influence of the Adsorbent upon Adsorption in Solution

The amount adsorbed has hitherto been referred to 1 gram of adsorbent. We have already briefly discussed in the case of gases (cf. p. 132), and must now consider more fully, that this mode of calculation is, strictly considered, not really practical; for the adsorptive power of a substance is determined by the amount adsorbed upon unit surface. Since the adsorbents used are mainly solid foams with a strongly developed inner surface, the development of the boundary surface can vary greatly. Only as long

[1] Zeitschr. f. Physik. **2**, 111 (1920).

as we employ a single homogeneous adsorbent is it a matter of indifference whether we refer to 1 gram or to 1 sq. cm. of surface. As soon as we compare two different adsorbents only the adsorption referred to 1 sq. cm., the true adsorptive power, is characteristic. In order to compare true adsorptive powers, we should have to know the specific surface, that is, the surface developed by 1 gram of adsorbent. It is a serious and very evident gap in capillary chemistry that no method is available to determine this specific surface, i.e. the inner surface of an adsorbent. If, however, two adsorbents differ only in the extent of their surfaces, but not in their true adsorptive power, then, as Mecklenburg [1] showed, the following rule must be true for their adsorption isothermals. The two adsorbents compared are to be exactly similar, as also their interfacial tensions and the manner of its dependence upon the concentration of the solute. Hence the same amount of solute must be adsorbed by both upon the square centimetre of surface from the same equilibrium concentration in the solution. Referred to the gram of adsorbent, the amount adsorbed will be correspondingly greater upon the adsorbent with the larger specific surface, and further, as is easily seen, the amounts adsorbed per gram must quite generally be in the ratio of the specific surfaces of the adsorbents. If therefore we have at concentration c for adsorbent 1 the amount adsorbed a_1, and for adsorbent 2 the amount a_2, and for c' correspondingly a_1' and a_2', then we have

$$a_1 : a_2 = a_1' : a_2' = \ldots \qquad (1)$$

It follows from this, *that if the ordinary adsorption isothermal is valid, the log a, log c straight lines must be strictly parallel to one another for the various adsorbents*; *the exponent* $\frac{1}{n}$ *has exactly the same value for all.* If more generally we consider the general adsorption curves, they must be *affine*; we can pass from one curve to another by multiplying the ordinates of the one by a constant factor.

Mecklenburg was able to show the existence of *affine adsorption curves* in a number of cases of adsorption in aqueous solution, for example,[2] in the case of various samples of stannic acid (adsorbed substance phosphoric acid) and of a number of ferric hydroxide gels (adsorbed substance arsenious acid) which differed from one another in the temperature at which they were precipitated by NH_3. If therefore we have affine adsorption curves, we may conclude with some degree of probability that the adsorbents in question are similar in nature and only differ in specific surface. Whether the converse conclusion quite holds, that non-affine adsorption isothermals mean difference in capillary nature, is an open question. One might imagine

[1] Zeitschr. f. physik. Chemie, **83**, 609 (1913).

[2] These examples are given here with caution, since strictly speaking they do not belong to the case, hitherto considered, of adsorption of undissociated substances by undissociated adsorbents. The following further examples may be referred to. *L. Wöhler* and *Streicher* [Ber. d. deutsch. chem. Ges. **46**, 1720 (1913)] made preparations of $IrCl_3$, which had very different colours: dark olive-green, yellow, brown-black; but probably differed only as regards the fineness of their state of division. In order to prove this, both the rate of settling and the adsorption of methylene blue were determined; these were largest in the case of the olive-green $IrCl_3$, and smallest in the case of the brown-black. A proof that we actually get affine adsorption curves would speak strongly in favour of the view that they are materially similar. *C. Kühn* [Kolloidzeitschr. **19**, 122 (1916)] found the same exponents in the case of the total adsorption (cf. p. 178) of brilliant green on certain silicates (decomposition products of pyroxenes, known as "Grünerde" and "Weisserde") in various states of division.

possibilities, in which affine behaviour would be masked in spite of similarity in chemical nature, but they are not probable.

Since we have no means of deciding generally whether the difference in adsorptive power of two adsorbents is to be referred to difference in true adsorptive power or to difference in specific surface area, many a question cannot yet be answered. However, the adsorptive power of charcoal exceeds that of other adsorbents to such an extent that it may be regarded as certain that in its case it is not merely a matter of an extraordinarily large surface, but also of a large true adsorptive power. Everything speaks in favour of the view that we are dealing with a property of carbon. It is true that the adsorption charcoals, wood and animal charcoal, are distinctly impure; but Pelet and Maccoli [1] have proved that no connexion exists between the nitrogen content of charcoals and their adsorptive power, and that no change in adsorptive power is produced when the nitrogen content is altered by energetic treatment with acids and alkalis. The adsorptive power of many other substances, such as talc, sulphur, meerschaum, may be made evident by very fine powdering, but it remains far below that of charcoal.[2] On the other hand, this fact, as already said, is no proof that adsorption is not a condensation upon a surface, for if the true adsorptive power is small, then the adsorption may remain small in spite of the largest specific surface.[3]

It is also an open question whether the fact that a crystalline solid has a smaller adsorptive power than an amorphous one of the same chemical nature, depends upon a difference in true adsorptive power or upon a difference in specific surface. It is, however, highly probable that we are dealing in the former case with the diminution of the specific surface resulting from crystallization. As examples of this behaviour we may give the following. The amorphous sulphur of the sulphur sols investigated by Odén [4] freely adsorbed various substances, salts such as NaCl and others; this property disappears almost completely when the sulphur has been transformed into the crystalline form by a little alkali. Further, amorphous sulphur coagulated out of a sulphur sol by neufuchsin contains an appreciable amount of adsorbed dye, which is again given up to the solution, when the sulphur itself in course of time gradually passes into the crystalline state.[5] Further examples are given on p. 189.

Undoubted regularities, holding for the true adsorptive power, are neither numerous nor well established. As in the case of the adsorption of gases, the adsorption from solutions by closely allied adsorbents does not appear to be specific. The adsorption exponent $\frac{1}{n}$ varies less than with gases, and hence one can often say that when a substance A is more strongly adsorbed by adsorbent 1 than substance B, and this more strongly than C, that then A will also be adsorbed more strongly by adsorbent 2 than B, and B more strongly than C. We therefore have

$$\left(\frac{a_1}{a_2}\right)_A = \left(\frac{a_1}{a_2}\right)_B = \left(\frac{a_1}{a_2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

[1] Bull. soc. chim. de France (4), **5**, 1011 (1909).
[2] *L. Michaelis* and *Rona*, Biochem. Zeitschr. **102**, 268 (1920).
[3] See the objections of *Dauwe*, Beiträge zur Physiologie und Pathologie, **6**, 426 (1905).
[4] "Der Kolloide Schwefel." Upsala, 1913, p. 178.
[5] *Freundlich* and *Hase*, Zeitschr. f. physik. Chemie, **89**, 460 *et seq.* (1915).

The best confirmation of this rule was given by L. Michaelis and Rona.[1] They obtained for the adsorbents blood-charcoal, talc, and sulphur,[2] the order of adsorption

n-octyl alcohol > secondary octyl alcohol > heptyl alcohol > tributyrin > acetone.

It is difficult to test formula (2) numerically, since no long-range adsorption isothermals have been determined. Nevertheless, in some cases the measurements are such that the amount of adsorbent is given which effects the same adsorption with the same adsorbed substance. We have therefore values of a for different adsorbents with equal c, which can straight-away be compared like a values; that the c values are different for different adsorbed substances is comparatively unobjectionable, if the adsorption exponent $\frac{1}{n}$ is not too different. We then get the following values :—

TABLE 64

Adsorption on various Adsorbents. Room Temp.

$$\left(\frac{a_{\text{charcoal}}}{a_{\text{talc}}}\right)_{n\text{-octyl alcohol}} = 420$$

$$\left(\frac{a_{\text{charcoal}}}{a_{\text{talc}}}\right)_{n\text{-heptyl alcohol}} = 590$$

$$\left(\frac{a_{\text{charcoal}}}{a_{\text{talc}}}\right)_{\text{tributyrin}} = 460$$

We see that blood-charcoal adsorbs about 500 times more strongly than talc, and this was the next best adsorbent. With a number of other adsorbents such as kaolin, ferric hydroxide, and silicic acid, the adsorption was not detectable. A further example may be given; according to L. and P. Wöhler and Plüddemann,[3] benzoic acid is adsorbed by red and also by heated iron oxide (as it is by charcoal) about ten times as strongly as acetic acid; further, B. Schulz [4] found the same order for a number of organic acids—picric, salicylic, benzoic, oxalic, and others—with charcoal, silk, and aluminium hydroxide as adsorbents.

This rule may be explained as follows. The adsorption equilibrium is conditioned by the attraction between the adsorbent and the molecules of the adsorbed substance on the one hand, and by the attraction between these and the molecules of the solvent on the other. If the attraction of the adsorbent is not very specific, but that between the molecules of the adsorbed substance and those of the solvent is highly so, if therefore very different amounts of work are required to remove a mol of the adsorbed substance from the interface into the interior of the solvent, then the influence of the adsorbent will recede into the background. We have the same order of adsorption with different adsorbents.

The existence of this rule, and the comparatively small variability of the adsorption exponent $\frac{1}{n}$, make it permissible to speak, with reserve, of one substance being more adsorbable than another, as will frequently be done in what follows:

It is however by no means necessary that the attraction of the adsorbent

[1] *loc. cit.* p. 187.
[2] Sulfur præcipitatum (sol. in CS_2).
[3] Zeitschr. f. physik. Chemie, **62**, 664 (1908).
[4] "Über die Adsorption in Lösungen." Diss., Königsberg, 1908, p. 39.

should be of subsidiary importance. It may be quite in evidence, and may even become of prime importance, so that a specific adsorption results (cf. p. 120). Insight into the properties which condition the true adsorptive power of an adsorbent would be most easily gained, if we had as an adsorbent an organic substance, the properties of which could be varied according to plan by substitution, etc.

An advance in this direction is given us by the experiments of Barger [1] on the adsorption of iodine by different adsorbents. It appears that the long-known fixation of iodine by starch with formation of blue "iodide of starch" is only one example of a widespread phenomenon. A large number of organic substances in particular are, as Barger could show, able to take up iodine with production of a blue colour. That in the case of this loose association we are dealing with an adsorption is very probable; the processes are reversible, equilibrium is quickly reached, and the ordinary adsorption isothermals were found in the case of starch,[2] saponarin [3] (a glucoside), and amorphous cholic acid.[3] Some sort of chemical change must however take place, if we get the blue colour instead of brown in a solution. It is not certain upon what this difference in colour depends. The most probable supposition is, that we are dealing in all cases with a combination of the iodine with molecules of the solvent, even though the blue or violet iodine is closer to the pure iodine molecule than the brown.[4] Harrison [5] would prefer to regard pure iodine as the adsorbed substance.

The circumstance must further be taken into account that the presence of KI is necessary for the adsorption of iodine.[6] Hence we might at first regard a compound of I_2 and KI as the substance adsorbed. Against this view Barger and Miss Field pointed out that other salts as well, particularly those with multivalent kations such as $BaCl_2$, $LaCl_3$, are able to take the place of KI. This would favour the view that we are dealing with a property to be discussed later, by which a salt increases the adsorptive power of an adsorbent. It would be no less important to know whether the power of certain substances, such as furfurol and others, to diminish the blue coloration with low iodine concentrations, depends upon a displacement.[7]

The fact is generally very pronounced that an amorphous or extremely fine crystalline state of the adsorbent is essential for the adsorption of I_2. In the case of starch this condition is fulfilled. But the organic substances examined by Barger—particularly xanthone and flavone and their derivatives—can be either amorphous or finely crystalline or coarsely crystalline, and the majority of them adsorb iodine only when they are amorphous (or finely crystalline). This condition is usually attained as follows. We are dealing with substances which are difficultly soluble in water, but easily soluble in organic solvents, such as alcohol. If an alcoholic solution of

[1] Journ. Chem. Soc. **89,** 1210 (1906); *Barger* and Miss *Field*, *ibid.* **101,** 1394 (1912); *Barger* and *Starling*, *ibid.* **107,** 411 (1915).

[2] Among others *F. W. Küster*, Lieb. Ann. **283,** 360 (1894); *Katayama*, Zeitschr. f. anorg. Chemie, **56,** 209 (1908); *Harrison*, Kolloidzeitschr. **9,** 5 (1911).

[3] *Barger* and Miss *Field*, *loc. cit.* under [1].

[4] See e.g. *B. Waentig* [Zeitschr. f. physik. Chemie, **68,** 513 (1910)]. Incidentally the appearance of the blue colour only makes the phenomenon particularly plain. But there are unquestionably many cases of adsorption of I_2 in existence, in which it is taken up with a brown coloration (see e.g. *Siegrist*, "Contributions à l'étude des phenomènes d'adsorption." Diss., Lausanne, 1910, p. 46 *et seq.*

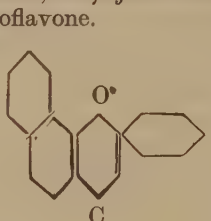
[5] *loc. cit.* under [2].

[6] *Mylius*, Ber. d. deutsch. chem. Ges. **20,** 689 (1887)

[7] *Clementi*, Arch. d. Farmac. sperim. **20,** 258 (1915), cited from Chem. Zentralbl., 1916, **1,** 179.

such a substance is poured into excess of water, the solid separates at first in the amorphous condition, and then gradually passes over into the crystalline state. If the water originally contained $I_2 + KI$, the flakes at first precipitated are coloured deep blue, but give up the I_2 again as they change into colourless crystals.

The power of adsorbing iodine with the production of a blue colour seems to be associated, in the case of the majority of these organic substances, with a definite constitution. They have—as far as we are dealing with the derivatives of xanthone, flavone, and allied substances, to which also saponarin belongs—*crossed, conjugated double bonds*, that is, a grouping of bonds as in α-naphthoflavone.



If a double bond is destroyed by reduction, the power in question disappears.

We have here apparently a good example of the fact that the surface attraction which causes adsorption is to be referred to chemical forces acting between molecules. For we ascribe in some measure to such a constitution free valencies, and it at once suggests itself that the reason for the adsorption of iodine is to be found in their presence. This conclusion is obviously not irresistible, since as long as we know nothing for certain regarding the specific surface, this constitution might also favour the appearance of the amorphous form with a strongly developed surface.

The adsorptive power of these adsorbents is altered in a regular manner by the introduction of various groups; aryl groups decidedly increase it. These also enhance the adsorbability of a dissolved substance (cf. p. 197). It would therefore appear that *the power of adsorption of an adsorbent and the adsorbability of a dissolved substance are influenced in the same direction by a certain constitutional change.* This is not improbable; under comparable conditions an adsorbent will have greater adsorbing power, the greater its interfacial tension against the solvent, the more therefore this tends to become smaller; aryl groups almost certainly raise the interfacial tension of the adsorbent against water. Put the other way round, dissolved substances which lower the interfacial tension of water are likewise only such as have not too great an affinity for water; for capillary activity and tendency to solution are frequently antibatic to one another (cf. p. 70), and aryl groups again diminish this affinity, and therefore enhance the capillary activity and so the adsorbability.

The phenomena under discussion are in other respects very complex. Some of these substances are more sensitive than starch; such are, for example, indenoflavone and α-naphthoflavone; the latter still shows a blue coloration in a 0·0067 millinormal solution of iodine, if the liquid contains multivalent kations. Others, however, are insensitive, and show the blue coloration only in comparatively concentrated I_2 solutions. Further differences are exhibited in the fact that a great number of sub-

stances only take up iodine in the manner above described when they are amorphous (or finely crystalline), while others, for example flavone, 6- and 7-methyl flavone, and also cholic acid, change from blue amorphous flakes into larger crystals likewise containing iodine, and generally blue. Here the crystals also adsorb iodine.

We might gain the impression that this taking-up of iodine is a case of very specific adsorption. But this is not yet settled, for iodine is a substance having a strong general capacity of being adsorbed,[1] which becomes particularly plain in this case by colour-change, and it is quite possible that these organic adsorbents also adsorb other substances, the detection of which is less easy.

An important group of inorganic adsorbents is constituted by a number of hydroxides and acetates, such as beryllium hydroxide,[2] hydrated oxides of iron,[3] and zirconium,[4] stannic acid,[5] lanthanum,[6] and praseodymium [7] acetates, and others. They too in general only adsorb strongly when amorphous (or finely crystalline). This is particularly evident in the case of the adsorption of iodine by the acetates above mentioned. But it also appears in the fact that the adsorption is only considerable when the substances are freshly precipitated, and not when they are used in an already prepared form. They adsorb especially iodine—the two acetates thereby exhibit the blue coloration—and also substances such as boric acid, phosphoric acid, arsenious acid, and others. In most cases the ordinary adsorption isothermal holds. For the adsorption of iodine by hydrated zirconium oxide and lanthanum acetate the adsorption exponent has the value 1. After what was said previously (cf. p. 127) the van 't Hoff laws are then also valid in the adsorption layer. That the interaction between arsenious acid and hydrated ferric oxide, which is so important toxicologically, has the character of an adsorption was first pointed out by W. Biltz.[8]

Adsorption by Several Adsorbents

The simultaneous adsorption by several adsorbents may be simply calculated, if they do not act upon one another. This may be assumed with some probability, if their electrical charges are not greatly different. If they are thus to a great extent independent of one another, we can suppose with Mecklenburg [9] that they also adsorb independently of one another. If adsorbent A is present in amount m_A and adsorbs the amount x_A which is in equilibrium with a solution of concentration c, and with the same concentration an adsorbent B present in amount m_B adsorbs x_B, then with the same concentration, same volume, and the amounts m_A and m_B present, we have the amount $x_{AB} = x_A + x_B$ adsorbed in equilibrium. We can therefore obtain the adsorption isotherm for x_{AB} by adding together the values of x_A and x_B for each value of c. This was confirmed by experi-

[1] See e.g. *Guichard*, Compt. rend. **151**, 236 (1910); *Pelet* and *Siegrist*, Bull. soc. chim. France (4), **5**, 626 (1909).
[2] *Bleyer* and *Br. Müller*, Arch. f. Pharm. **251**, 304 (1913); *Bleyer* and *Paczuski*, Kolloidzeitschr. **14**, 295 (1914).
[3] *Lockemann*, *loc. cit.* p. 178.
[4] *Wedekind* and *Rheinboldt*, Ber. d. deutsch. chem. Ges. **47**, 2142 (1914).
[5] *Mecklenburg*, *loc. cit.* p. 186.
[6] *W. Biltz*, Ber. d. deutsch. chem. Ges. **37**, 719 (1904).
[7] *Orlow*, Chemiker Zt. **31**, 45 (1907).
[8] Ber. d. deutsch. chem. Ges. **37**, 3138 (1904).
[9] *loc. cit.* p. 178.

ments of Lachs,[1] for the adsorption of acetic acid on charcoal and wool, and other substances.

If we desire to know what equilibrium is attained in a solution containing the amount of solute y when amounts m_A and m_B of adsorbents A and B are added, the graphical method of Mecklenburg described on p. 178 may again be used. The hypotenuse of the isosceles right-angled triangle with sides equal to y cuts the adsorption curves at the desired points.[2] Lachs[3] has shown how this method may also be applied to the case in which the adsorbent is present in any amount.

The Dependence of Adsorption upon the Solvent

A certain general view of the dependence of adsorption upon the solvent and solute is gained by again assuming, as on p. 180, that the general σ, c curve holds for the interface solid—liquid. In order first of all to compare the behaviour of various substances as solvents, we may combine various σ, c diagrams, as has been done in Fig. 37 (using different scales for the concentration on the axis of abscissæ). We then see first that a strong depression of σ, and hence strong adsorption, is only probable in the case of solvents with large interfacial tension, and not in the case of those with small. Experiment entirely confirms this; water is characterized by a high surface tension and by a high interfacial tension against other liquids.

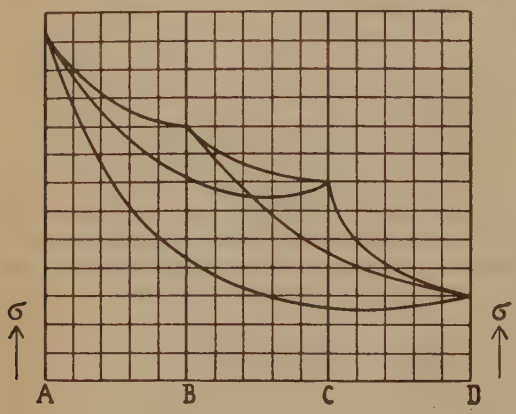


Fig. 37.

We may therefore ascribe to it also a large interfacial tension against solids, especially hydrophobic solids. The same is true for sulphuric acid. In actual fact strong adsorptions have only been found in the case of water, and fairly strong ones in the case of sulphuric acid. On the other hand, adsorption is low in organic liquids such as benzene, alcohol, ethyl ether, and others, in the case of which we may assume for similar reasons a low interfacial tension against solids. Table 65 gives a numerical picture of this behaviour. The a values are not compared in it, since they were mostly obtained by excessive extrapolation, but the a values at $c = 0{\cdot}01$ mol per litre are given. The adsorption exponent $\frac{1}{n}$ is as a rule not so greatly different as to render a comparison of this kind inadmissible. It is in agreement with this fact that the separation of solvent and solute, described in connexion with capillary analysis (cf. p. 213), is observed either not at all, or only to a

[1] Zeitschr. f. physik. Chemie, **91**, 155 (1916); Spraw. z posied. Tow. Nauk. Warsz. **6**, 508 (1913); **7**, 1 (1914).

[2] The "coexistence principle" applied by *Lachs*, which is also intended to solve this problem, is only approximately correct at higher concentrations.

[3] Spraw. z posied. Tow. Nauk. Warsz. **10**, 806 (1917).

TABLE 65 [1]

Adsorption on Blood-charcoal in different Solvents. Room Temp.

Solvent.	Adsorbed Substance.	*a.*
Water	Benzoic acid	3·27
Benzene	„ „	0·54
Ethyl ether	„ „	0·30
Acetone	„ „	0·3
Water	Picric acid	1·31
Ethyl alcohol	„ „	0·767
Benzene	„ „	0·486
Water	Bromine	4·73
Conc. sulphuric acid	„	2·48
Ethyl ether	„	1·36

very slight extent, in the case of solutions of dyes in organic solvents (e.g. nitrobenzene, etc.).[2]

Polanyi's theory leads to a more strict connexion (cf. p. 194).

On account of the low adsorption in organic solvents, adsorbed matter can be removed from the surface of an adsorbent by washing the charged adsorbent with organic liquids. This is frequetly important, since it is often practically impossible by any other means to make the adsorbed substance susceptible to analytical detection. For if the substance has been adsorbed in aqueous solution by a large amount of adsorbent, so that its concentration in the solution has fallen below the limits of analysis, washing out the adsorbent with fresh water can only yield concentrations which are still lower than before, for they are in equilibrium with still smaller amounts of adsorbed substance. The substance could therefore only be detected by evaporating large quantities of wash-water. On account of the much smaller adsorption, the adsorbed substance passes, on the other hand, freely into an organic solvent with which the adsorbent is washed. This can be excellently tested with charcoal, with which a dye has been completely removed from aqueous solution. Upon this depends the ease with which dyed fibres can often be bleached by organic liquids.[3]

The rule mentioned on p. 187 concerning a certain independence of

[1] From measurements by Freundlich, *loc. cit.* p. 172.

[2] *Losev*, "Über die Adsorption der Farbstoffe durch Kohle und Fasern." Diss. Leipzig, 1907, p. 64. Further examples of the stronger adsorption in water than in organic solvents are to be found in *Vignon*, Compt. rend. **148,** 844 (1909) (Adsorption of picric acid on fibres in different solvents), *Freundlich* and *E. Posnjak*, Zeitschr. f. physik. Chemie, **79,** 168 (1912) [the values found there in acetone for succinic acid, benzoic acid, *m*-nitro-benzoic acid, salicylic acid, picric acid, must be compared with those found by *Freundlich* (*loc. cit.* p. 172) in water]; *Gustafson*, Zeitschr. f. physik. Chemie, **91,** 402 (1916). *Robinson* [Proc. Camb. Phil. Soc. **15,** 548 (1910)] interprets the taking-up of HCl and HBr by sugar, cellulose, and the like in solutions of chloroform—carbon tetrachloride mixtures as an adsorption. *Schilow* and Frl. *Lepin* (*loc. cit.* p. 123) have investigated the adsorption, in particular however of electrolytes, in mixed solvents by charcoal.

[3] *Freundlich* and *W. Neumann*, Zeitschr. f. physik. Chemie, **67,** 538 (1909). It should be remarked here that *Th. Graham* and *A. W. Hofmann* [Lieb. Ann. **83,** 39 (1852)] already used this phenomenon in the year 1852 for analytical purposes. The strongly adsorbable strychnine can be removed from aqueous liquids by charcoal (the problem at the time was to prove the presence of strychnine in beer). By subsequent washing of the charcoal with alcohol the strychnine is removed.

adsorption on the nature of the adsorbent appears also to hold in the case of various solvents. For example, according to experiments of Appleyard and Walker,[1] the ratio

$$\left(\frac{a_{\text{charcoal}}}{a_{\text{silk}}}\right)_{\text{picric acid}}$$

for a concentration $c = 0{\cdot}01$ mol per litre is in water $= 7{\cdot}3$, in alcohol $= 5{\cdot}2$.

We may therefore, after the above discussion, legitimately say that a greater adsorption takes place in one solvent than in another.

The Dependence of Adsorption in Solutions upon the Nature of the Dissolved Substance

Concerning the influence of the nature of the dissolved substance, Fig. 37 allows of some such conclusion as the following. Substances with a high interfacial tension will, when dissolved, cause a small depression in the interfacial tension of the solvent, and will therefore be weakly adsorbed, while substances with a small interfacial tension will cause a strong depression and hence will be strongly adsorbed. There is, however, as previously pointed out (p. 64), no parallelism between the surface tension of the pure materials and the depression of the surface tension of the solvent which they cause. Nevertheless, it agrees with what has been said, that a substance with a high interfacial tension such as sulphuric acid is weakly adsorbed in water, whereas we must ascribe small interfacial tension to the strongly adsorbable organic liquids. And the rule may be formulated: *If in one substance as solvent another substance is strongly adsorbed, the solvent itself, when in solution, will be weakly adsorbed, and vice versa.*

Polanyi was able to deduce this rule from his formula (2) (on p. 185). Let the solubility L of an adsorbed substance be practically equal in two solvents 1 and 2, and let solvent 1 be much more adsorbable than solvent 2, then

$$\varepsilon_{M_1}\frac{V_A}{V_{M_1}} > \varepsilon_{M_2}\frac{V_A}{V_{M_2}}.$$

In order that the adsorbed substance may have the same adsorption potential ε_A we must have

$$RT\log\frac{L}{c_1} < RT\log\frac{L}{c_2},$$

hence

$$c_1 > c_2$$

that is, the concentration of adsorbed substance which is in equilibrium in a strongly adsorbable solvent with a definite amount adsorbed, is greater than that which is in equilibrium with the same amount in a weakly adsorbable solvent. Hence adsorption is weaker in the more strongly adsorbed solvent.

If, on the other, hand we have solvents of approximately equal adsorbability (as will frequently be the case with various organic solvents), but an adsorbed substance which is soluble in them to different degrees, then we can put in formula (2), p. 185, the term

$$\varepsilon_M\frac{V_A}{V_M}$$

[1] *loc. cit.* p. 172.

approximately constant. Then for equal adsorbed amounts of the same substance the equilibrium concentration in the solution must be proportional to the solubility; in the solvent in which the substance is more soluble it will also be less adsorbed.

This was well confirmed by Lundelius'[1] experiments. He measured the adsorption on blood-charcoal of iodine in solutions in carbon disulphide, chloroform, and carbon tetrachloride, in which three liquids the iodine dissolves with a violet colour. The isothermals plotted logarithmically were perfectly parallel, and we can therefore compare the equilibrium concentrations for any desired amount adsorbed. The result was

$$c_{CS_2} : c_{CHCl_3} : c_{CCl_4} = 4{\cdot}5 : 2 : 1,$$

while for the solubilities[2] at 14·5° in relative measure we find

$$L_{CS_2} : L_{CHCl_3} : L_{CCl_4} = 69{\cdot}1 : 14{\cdot}3 : 8{\cdot}1 = 4{\cdot}8 : 1{\cdot}8 : 1.$$

The distinction between capillary active and capillary inactive solutions is again helpful. To the capillary inactive solutions belong in the first place solutions in organic solvents, in which other dissolved substances, such as organic substances, halogens, etc., are only weakly or moderately adsorbed. In dilute solution the adsorption isothermal holds generally. It has been observed that, as a first approximation, kindred substances such as benzoic acid and its derivatives, phenol, aromatic aldehydes, and the like, are equally adsorbed in equimolecular concentration.[3] This recalls the behaviour of these solutions as regards their surface tensions (cf. p. 56), although in that case it was a question of the increase in σ, in this of a positive adsorption. Salts especially are weakly or only moderately adsorbed in aqueous solution, particularly the inorganic, as also are the inorganic acids and bases, which must be discussed later (cf. p. 201).

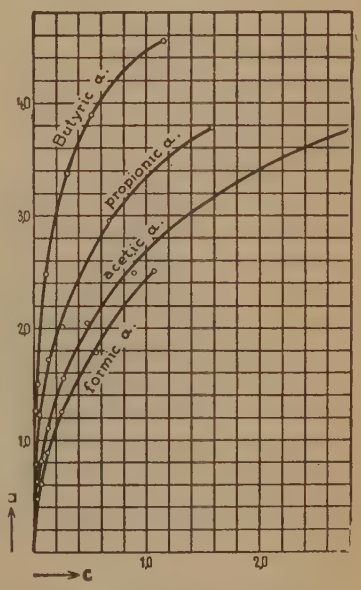


Fig. 38A.—Adsorption Isothermals of Aqueous Fatty Acid Solutions.

Again, we have capillary active solutions in the case of aqueous solutions of many organic substances, the fatty acids, urethanes, the aromatic acids, the phenols, camphor, alkaloids, dyes, and many others, and then also the halogens.

Here we meet afresh with Traube's rule (cf. p. 64). *The adsorption of organic substances from aqueous solutions increases strongly and regularly as we ascend the homologous series.* Figs. 38A and B show the a, c curves and log a, log c straight lines for the adsorption of formic, acetic, propionic, and n-butyric acids from aqueous solution by blood-charcoal[4]; the similarity with

[1] Kolloidzeitschr. **26**, 145 (1920).
[2] *Bruner*, Zeitschr. f. physik. Chemie, **26**, 145 (1898).
[3] See e.g. *Freundlich* and *Posnjak*, *loc. cit.* p. 193.
[4] From measurements by *Freundlich*, *loc. cit.* p. 172.

Figs. 12 and 13 is striking. For the purpose of numerical formulation we compare, as on p. 64, with given a the concentration c_n of the one member with the concentration c_{n+1} of the next higher member of the homologous series. $\frac{c_n}{c_{n+1}}$ is approximately constant and about 2 to 3, as appears from the following tables. We can naturally use also the quantity $\frac{a_{n+1}}{a_n}$ for comparison (cf. p. 66), as has been done in Table 67. q has in general a value of about 1·5.[1]

TABLE 66 [2]

Traube's Rule for the Adsorption of Fatty Acids by Blood-charcoal
t = 25°

Adsorbed Substance.	c Mol/Litre for a = 1·26 millimol/gm. Charcoal.	q.
Formic acid	0·251	—
Acetic acid	0·169	1·48
Propionic acid	0·056	3·01
n-Butyric acid	0·016	3·48

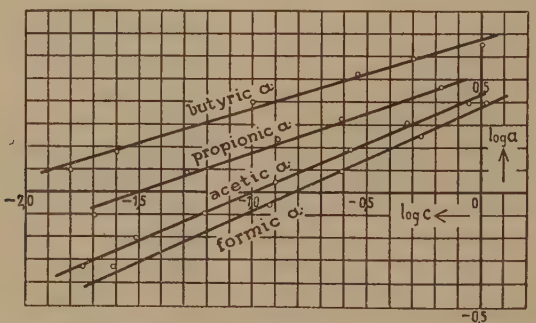


FIG. 38B.—Adsorption Isothermals of Aqueous Fatty Acid Solutions plotted logarithmically.

TABLE 67 [3]

Traube's Rule for the Adsorption of Fatty Acids by Blood-charcoal
t = 25°

Adsorbed Substance.	a millimol/gm. Charcoal for c = 0·1 Mol/Litre.	q.
Formic acid	0·79	—
Acetic acid	1·00	1·26
Propionic acid	1·55	1·55
n-Butyric acid	2·43	1·56

[1] As a further example the adsorption of isobutyl alcohol and isoamyl alcohol by charcoal may be mentioned (*van Duin, loc. cit.* p. 175).

[2] From measurements by *Freundlich, loc. cit.* p. 172.

[3] From measurements by *Freundlich, loc. cit.* p. 172.

That p (and q) are somewhat smaller than in the case of the lowering of σ depends upon the fact that in the one case we are comparing the depression of the surface tension, and in the present case the amount adsorbed; the connexion between the two, which is not yet known quantitatively. would have to be taken into account.

TABLE 68 [1]

Traube's Rule for the Adsorption of Urethanes by Blood-charcoal. Room Temp.

Adsorbed Substance.	c Mol/Litre for $a = 1{\cdot}585$ millimol/gm. Charcoal.	p.
Methyl urethane	0·0437	—
Ethyl urethane	0·0190	2·3
Propyl urethane	0·0093	2·0
Isobutyl urethane	0·0050	1·9

As regards the theory of Traube's rule, we may apply what was deduced on p. 68; we have only to put in place of the solid—gas interface the solid—liquid one. Evidently, the differences in the specific attraction between adsorbent and adsorbed substance are of little importance as compared with the differences in the amounts of work which are necessary to bring 1 mol of the adsorbed substance from the interface into the interior of the solution. Further, we may assume that the CH_2 chains lie entirely in the interface.

Certain constitutive influences which have been observed in the case of a number of adsorbents (charcoal, fibres, iron oxide, and others) are very striking. The aromatic substances (benzoic acid and its derivatives, aniline, phenol, etc.) are in general more strongly adsorbed than the aliphatic; hence probably the strong adsorption of the alkaloids, dyes, and the like. The introduction of the sulphonic acid group to a great extent annuls this increase in the capillary activity. Benzene Gk_a sulphonic acid and sulphanilic acid are only as strongly adsorbed as propionic acid. Halogen- and nitro-derivatives of benzoic acid, on the other hand, are on the whole adsorbed better. The following table gives a general picture of the adsorption of various substances by blood-charcoal. Again the adsorption values a are not given (cf. p. 192), but instead the amounts adsorbed at a concentration of $c = 0{\cdot}01$ mol/litre.

How far does the adsorbability of a substance (that is, its capillary activity, at the interface solid—liquid) run parallel with its capillary activity at the interface liquid—gas? A symbasis of this kind is not necessary; the considerations on page 89 for the interface liquid—liquid can be immediately applied to the interface solid—liquid. But it is worth exploring how far this parallelism is present. That the Traube rule holds at both interfaces for the fatty acids and urethanes has already been pointed out. The parallelism is evident for the three chloro-acetic acids. The difference in capillary activity as regards the surface.

[1] From measurements by *Rona* and *von Tóth*, Biochem. Zeitschr. **64**, 288 (1914). The comparison is rendered more difficult by the fact that the experiments did not extend over a considerable range of concentration. Fortunately the adsorbed amounts lie fairly close to one another (at about 1·6 millimol/gm. charcoal); c values can therefore be compared for a given a, as has been done in the table.

TABLE 69 [1]

Adsorbability of various Substances in Aqueous Solutions by Blood-charcoal. $t = 25°$, except in the case of Bromine, where it is 0°

Adsorbed Substance.	a millimol/gm. Charcoal.
Acetic acid	0·37
Propionic acid	0·57
n-Butyric acid	1·04
Monochloro-acetic acid	0·76
Dichloro-acetic acid	0·74
Trichloro-acetic acid	0·66
Succinic acid	1·30
Benzoic acid	3·27
Salicylic acid	3·04
Picric acid	1·31
Sulphanilic acid	0·72
Phenol	1·86
Aniline	2·40
Bromine	4·73

tension of their aqueous solutions is small; the dichloro-acid (in a concentration between 0·2 and 0·8 mol) lowers σ somewhat more strongly than the two others.[2] For adsorption by charcoal (see Table 69) and by hide-powder,[3] the adsorption isothermals lie in part so near together that they intersect; at higher concentrations the dichloro-acid is most strongly adsorbed, the mono-substituted, however, in contrast to the behaviour in the case of surface tension, more strongly than the tri-substituted. The symbasis appears also especially in the rule to be discussed later (cf. p. 203), that acids and alkalis are more strongly adsorbed than their salts, just as they also depress the surface tension of water more strongly than their salts (cf. p. 60).

There is, however, a series of substances which are strongly and even very strongly adsorbed in aqueous solution, but only depress the surface tension of water very slightly; these are, for example, acids such as succinic acid, aromatic compounds such as benzoic acid and its derivatives, dyes, alkaloids, and other substances. Also the sugars [4] (glucose, lactose, cane-sugar) are comparatively well adsorbed—about as strongly as dichloro-acetic acid—and yet they raise the surface tension of water (p. 56). If we attempt to decide as to which substances show parallelism and which do not, the results so far available indicate that volatile substances (such as the fatty acids) present the parallelism, and difficultly volatile (such as succinic acid, benzoic acid) do not. One might explain this as follows. In the case of volatile substances, the part of the capillary layer lying towards the vapour side is also filled to a great extent with molecules of these capillary active substances; in the case of non-volatile bodies this is not the case to the same extent. The lowering of the surface tension caused by the enrichment at the surface is therefore less in the case of the non-volatile substances than

[1] According to measurements by *Freundlich, loc. cit.* p. 172.
[2] See *Drucker*, Zeitschr. f. physik. Chemie, **52**, 641 (1905).
[3] *Stiasny*, Collegium 1908, p. 117.
[4] *R. O. Herzog, Rona* and *Michaelis, loc.cit.* p. 175; further *Wiegner*, Kolloidzeitschr. **8**, 126 (1911).

in the case of the volatile. Naturally, the specific attraction between adsorbent and adsorbed substance must also be reckoned with here.

The relation to the tendency to dissolve is strongly marked in the case of adsorption by solid adsorbents. The strongly adsorbable aromatic substances are for the most part difficultly soluble in water; for the adsorption of alkaloids by various adsorbents, the symbasis between solubility and adsorbability was shown by Berczeller and Csáki.[1] The weakly adsorbable inorganic salts, acids, and bases are easily soluble. The solubility of organic substances in organic solvents is likewise great, while their adsorbability from them is small. However, exceptions also exist here, which show plainly that in the case of adsorption we are not, as in the case of solubility, dealing only with the interaction between the molecules of solvent and solute, but also with that between adsorbent and solute. Thus it is true that the greater solubility of benzene sulphonic acid corresponds to its lesser adsorbability; but sulphanilic acid is less strongly adsorbed than benzene sulphonic, although possessing a much smaller solubility; the very soluble mellitic acid is strongly adsorbed.[2]

The argument on p. 194, concerning the antibasis of solubility and adsorbability of one and the same adsorbed substance in different solutions, leads to a like antibasis for different adsorbed substances in the same solvent, assuming that the molecular volumes of the adsorbed substances do not differ too widely.

Adsorption in a Solution of Several Substances

A series of investigations[3] makes it possible to form a picture, albeit a rough one, of the simultaneous adsorption of several substances. The following points must be emphasized as important:

1. The velocity of adsorption, as far as we know at present, has the same character as the velocity of adsorption in pure solution. It is great; that is, in the case of finely powdered adsorbents with not too fine pores the equilibrium is reached in a few minutes. This is also true for the case in which a substance added subsequently displaces a substance previously adsorbed, even when the latter is the more adsorbable. That the same equilibrium is reached independently of the order of adsorption may be illustrated by the following example. In the first case a benzoic acid solution was shaken with charcoal and succinic acid added; the total acid concentration after equilibrium had been reached amounted to 0·1968 equivalents; when, on the other hand, the succinic acid was first added and then the benzoic, the concentrations being the same as before, the equilibrium concentration was 0·1978 equivalents (Masius).

2. In the case of the adsorption of two active substances by one adsorbent a mutual displacement usually takes place; each of the two substances will therefore be more weakly adsorbed in the mixture than if it alone were present in the solution at the same concentration (but see p. 642). The displacement depends greatly upon the concentration of the substance, inasmuch as the one present in greater concentration is in general more strongly displaced. Still more important is the influence of adsorbability; the substance more adsorbable in pure solution is able to displace a more

[1] Biochem. Zeitschr. **53**, 238 (1913).

[2] These data are from *Freundlich's* measurements, *loc. cit.* p. 172.

[3] *L. Michaelis* and *Rona*, Biochem. Zeitschr. **15**, 196 (1908); *Masius, loc. cit.* p. 177; further, *Freundlich* and *Masius, van Bemmelen*-Festschr. 1910, p. 88; *B. Schulz, loc. cit.* p. 188; *Freundlich* and *Poser, loc. cit.* p. 183.

weakly adsorbable one even when the former is present in considerably smaller concentration. Hence the order of adsorbability according to Traube's rule makes itself plainly felt. This appears from the following table; it contains results by Rona and v. Tóth [1] on the displacement of glucose from animal charcoal upon simultaneous adsorption of urethane.

TABLE 70

The Displacement of Glucose by Urethane on Adsorption of both by Blood-charcoal. Room Temp.

Displacing Adsorbent.	Conc. of Glucose, Mol/Litre. Before.	After.	$a_{\text{Glucose.}}$	Conc. of Urethane. Before.	After.	$a_{\text{Urethane.}}$
—	0·050	0·029	0·51	—	—	—
Methyl urethane .	0·050	0·037	0·32	0·072	0·031	1·0
Ethyl urethane .	0·050	0·040	0·25	0·074	0·021	1·3
Propyl urethane .	0·050	0·046	0·10	0·070	0·009	1·5
Isobutyl urethane	0·050	0·049	0·03	0·070	0·004	1·6

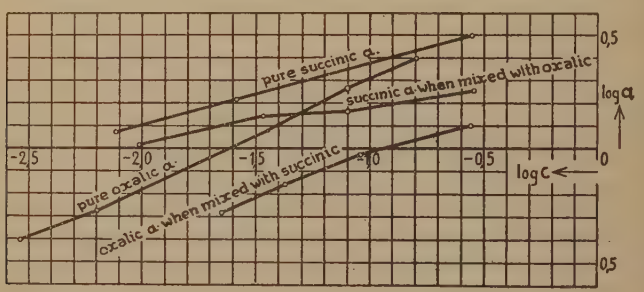


FIG. 39.—Adsorption Isothermals of Solutions of two Substances.

We thus get an excellent example of a "poisoning" which is the better defined the greater the difference in adsorbability. On account of the importance of these phenomena a further example from Masius may be given. While in pure oxalic acid solution an $a = 1{\cdot}25$ $\frac{\text{millimol}}{\text{gm.-blood-charcoal}}$ is in equilibrium with a concentration $c = 0{\cdot}085$ mol/litre, the presence of a concentration of 0·004 mol/litre of benzoic acid suffices to diminish the a of oxalic acid which again is in equilibrium with $c = 0{\cdot}085$, to 0·18 millimol/gm. charcoal.

In the case of a mixture of a capillary active adsorbed substance with a capillary inactive one, like a salt, the same relations appear as were described above (see p. 72) in the case of the influence of salts on the surface tension of aqueous aniline solutions; since the salts depress the tendency to dissolve of the capillary active substance, they increase its adsorbability. This has been recently proved by Wiegner, Magasanik, and Virtanen [2] for the influence of salts on the adsorption of fatty acids.

3. In general, the ordinary isothermal may be applied to each substance in a mixture, as appears from Fig. 39, which relates to an adsorption in

[1] *loc. cit.* p. 197.

[2] Kolloidzeitschr. **28**, 51 (1921).

approximately equivalent solution by blood-charcoal at room temperature; here also c is again in mol/litre, a in millimol/gm. charcoal. The adsorption exponent $\frac{1}{n}$ for the isothermal of a substance in a mixture is generally smaller than in pure solution. The substance more strongly adsorbed in pure solution is relatively as well as absolutely more strongly adsorbed in a mixture than the more weakly adsorbed body. These relations also hold when both substances are strongly adsorbed, for example, in the adsorption of benzoic and salicylic acids by blood-charcoal and fibrous alumina from aqueous solution.[1]

4. The total adsorption—calculated as the total number of mols independently of the nature of the separate substances—is frequently on the average about as great as if the more strongly adsorbable substance alone were present in the solution at the same concentration. This may be deduced from the experiments of Masius, and follows also quite plainly from measurements by Freundlich and Poser. This fact may be taken as a confirmation of the view of Reichinstein, given on p. 145, who puts the total number of molecules in the adsorption layer equal to a constant. As there remarked, this relation can only be taken as approximately valid.

The Adsorption of Strongly-dissociated Substances

The adsorption of strong electrolytes shows a number of peculiarities, so that in their case the assumption of an "electrical adsorption," differing from the ordinary capillary-chemical, has frequently been considered necessary. We will leave the question as to the correctness of this view open for the present, and simply ask to what extent is adsorption of electrolytes similar to that of undissociated or slightly dissociated substances, and to what extent does it differ therefrom? We shall always be dealing in the following with aqueous solutions.

In the case of single electrolytes or mixtures of the same we have usually to deal with equilibria which adjust themselves easily and, for the most part, rapidly. The ordinary isothermal is also true for electrolytes in dilute solution. This was shown in the case of the adsorption of chlorides, thiocyanates, and sulphates of the alkali, alkaline-earth, and earth metals by blood-charcoal by Rona and L. Michaelis[2]—they determined both the anion and kation content of the solution after adsorption; for the adsorption of H_2SO_4, KCl, KNO_3, K_2SO_4, and others by silicic acid, stannic acid, manganese dioxide, by van Bemmelen,[3] who also in part estimated both ions; for the adsorption of $Pb(NO_3)_2$, $Cu(NO_3)_2$, $CuSO_4$, $HgCl_2$, $AgNO_3$, Ag acetate by blood-charcoal, by H. Morawitz,[4] and of NH_4Cl, $(NH_4)_2SO_4$, $UO_2(NO_3)_2$, $Ce(NO_3)_3$, morphine hydrochloride by arsenic trisulphide powder, by Freundlich,[5]—in both cases the kation was determined analytically; in the case of NaCl, KCl, NH_4Cl, KCNS, KNO_3, K_2SO_4, $K_2Cr_2O_7$, K_2CrO_4, $K_4Fe(CN)_6$, K-salicylate, K-sulphanilate, K-oxalate, K-succinate

[1] See, besides *Masius*, especially *Freundlich* and *Poser*, *loc. cit.* p. 183; also the adsorption of methyl urethane in presence of glucose may be represented by the usual adsorption isothermal [*Rona* and *von Tóth*, Biochem. Zeitschr. **64**, 293 (1914)].

[2] Biochem. Zeitschr. **94**, 240 (1919).

[3] J. f. prakt. Chemie, **23**, 324, 379 (1881); Zeitschr. f. anorg. Chemie, **23**, 111 (1900) (in collaboration with *Klobbie*); **23**, 321 (1900); **36**, 380 (1903); Zeitschr. f. physik. Chemie, **18**, 331 (1895); "Die Adsorption," Dresden, 1910.

[4] Kolloidchem. Beihefte **1**, 301 (1910).

[5] Zeitschr. f. physik. Chemie, **73**, 385 (1910).

by fibrous alumina, by Ishizaka,[1]—in these cases the concentration of the ions after adsorption was measured.

The order of magnitude of the amount adsorbed is about 0·01–0·5 millimol per gram adsorbent, at a concentration of 0·01 to 0·1 mol/litre. The adsorption is therefore in general much smaller than in the case of capillary active substances; for the experiments much larger quantities of adsorbent are required. The adsorption exponent $\frac{1}{n}$ is often distinctly smaller than for the adsorption of non-electrolytes; this is particularly true of the dye salts, which indeed are usually also strong electrolytes. A comparison of Table 71 with Table 59 shows this clearly.

TABLE 71

Value of the Adsorption Exponent $\frac{1}{n}$ for the Adsorption of Electrolytes.

Solvent Water

Adsorbent.	Adsorbed Substance.	$\frac{1}{n}$	Observer.
Blood-charcoal	$Cu(NO_3)_2$	0·24	Morawitz [2]
,, ,,	Ag_2SO_4	0·33	,,
,, ,,	New fuchsin	0·186	Freundlich and Losev [3]
,, ,,	Patent blue	0·19	,, ,,
,, ,,	Crystal ponceau	0·15	,, ,,
Charcoal	Methylene blue	0·12	Pelet and Grand [4]
Arsenic trisulphide	NH_4Cl	0·203	Freundlich [5]
,, ,,	$UO_2(NO_3)_2$	0·095	,,
,, ,,	$Ce(NO_3)_3$	0·077	,,
,, ,,	New fuchsin	0·194	,,
Fibrous alumina	NaCl	0·620	Ishizaka [6]
,, ,,	NH_4Cl	0·610	,,
,, ,,	KNO_3	0·610	,,
,, ,,	K_2SO_4	0·523	,,
,, ,,	K-oxalate	0·360	,,
Metastannic acid	H_2SO_4	0·22	van Bemmelen [7]
Hydrated MnO_2	KOH	0·12	,, ,, [8]
Kieselguhr	Methylene blue	0·11	Pelet and Grand [4]
Calcined silicic acid	,, ,,	0·14	,, ,,
Wool	Patent blue	0·159	Freundlich and Losev [3]
Silk	New fuchsin	0·125	,, ,,
,,	Patent blue	0·163	,, ,,
Cotton	New fuchsin	0·253	,, ,,

The *general adsorption curve* also takes the course described on p. 180. For the adsorption of some electrolytes (HCl, NaCl, KCl, $CuSO_4$) by filter paper, Evans [9] found a decided maximum and subsequent fall in the amount adsorbed. The saturation in the adsorption of strychnine nitrate and dyes, which was mentioned on p. 183, should really have been left until this point, since these substances are strongly dissociated. The small value

[1] Zeitschr. f. physik. Chemie, **83**, 97 (1913).
[2] *loc. cit.* p. 201. [3] *loc. cit.* p. 182.
[4] Kolloidzeitschr. **2**, 41 (1907). [5] *loc. cit.* p. 201. [6] *loc. cit.* under 1.
[7] Journ. f. prakt. Chemie, **23**, 337 (1881). [8] *Ibid.* **23**, 347 (1881).
[9] J. Phys. Chem. **10**, 290, 1906.

of the adsorption exponent can therefore depend upon the fact that these strong electrolytes are already in the neighbourhood of saturation in small concentrations. Cases of negative adsorption have also been frequently described, first by Lagergren.[1] Although the measurements of Lagergren have not been confirmed, it is nevertheless probable that cases of negative adsorption occur, and that they may be explained on the basis of the general adsorption isothermal.

As in the case of the change in the surface tension of water by electrolytes, we meet here again the lyotropic series of the ions. Thus Rona and L. Michaelis[2] found for adsorption by blood-charcoal, with the same kation, the following order for the anions—

$$CNS > I > Br > Cl > SO_4.$$

The series in the case of kations was less striking, as the difference between K and Na was not particularly noticeable, while the adsorbability rose plainly with the valency:

$$Al > Ca, Mg > Na, K.$$

Heavy metal kations are frequently taken up more strongly than aluminium, a fact that will be discussed later in greater detail (cf. p. 211).

In the case of many adsorbents, the differences between these ions are apparently so greatly obliterated that the fact is again encountered (cf. p. 195) that closely allied substances in equimolecular solutions are approximately equally adsorbed, thus for example the kations $UO_2^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Ce^{\cdot\cdot\cdot}$ by arsenic trisulphide powder,[3] and NH_4 only a little less strongly. Organic ions are mostly adsorbed considerably more strongly. The aryl group strongly favours adsorption, the sulphonic group lessens it. Potassium salicylate and picrate were strongly adsorbed by fibrous alumina, K-succinate and K-sulphanilate less so. Strychnine nitrate, morphine hydrochloride, basic dyes, and salts of other organic bases such as aniline hydrochloride are much more strongly adsorbed by charcoal,[4] arsenic trisulphide[3] and others, than are inorganic salts.

Finally, we have a further regularity, which is already definitely developed in the case of the interfaces liquid—gas and liquid–liquid; acids and bases are much more active than their salts.[5] This is true, not only for the weakly dissociated organic acids, but also for the salts of strong acids. Some examples are given in Table 72 (p. 204), with blood-charcoal as adsorbent with approximately the same equilibrium concentration. The experiments with H_2SO_4 and sulphates we owe to Rona and L. Michaelis,[6] those with *o*-nitrobenzoic acid and its salts to Freundlich.[7]

We will now consider the differences in behaviour of strong electrolytes compared with that of non-electrolytes.

First of all comes the phenomenon that the anion and kation of the adsorbed substance are not adsorbed in equivalent amounts. This may go so far that the one ion is taken up practically quantitatively, while the other remains, likewise quantitatively, in solution. In other cases we encounter more or less considerable differences in the amounts of the two ions adsorbed. Of course, a real separation of the ions is impossible; in place of the ion adsorbed another enters the solution. This phenomenon

[1] *loc. cit.* p. 170. [2] *loc. cit.* p. 201.
[3] *Freundlich, loc. cit.* p. 201.
[4] *Freundlich,* Kolloidzeitschr. **1**, 321 (1907).
[5] See already *Lachaud,* Compt. rend. **122**, 1328 (1896).
[6] *loc. cit.* p. 201. [7] *loc. cit.* p. 172.

TABLE 72

Comparison of the Adsorption of Acids with that of their Salts

Absorbed Body.	c (Mol/Litre).	a Millimol/Gm. Ch.
H_2SO_4	0·0465	0·29
$(NH_4)_2SO_4$	0·0438	0·013
o-Nitrobenzoic acid	0·045	4·5
K-*o*-nitrobenzoate	0·045	0·6

was first observed by Knecht[1] in the adsorption of basic colouring matters by fibres, and then by Vignon[2] also for other salts by fibres, by v. Georgievics[3] for dyes on adsorbents such as clay and glass. It has been most thoroughly examined recently by L. Michaelis and Rona.[4]

Table 73 contains examples of equivalent adsorption along with such cases in which a large departure from equivalence is shown.

TABLE 73

Equivalent and Non-equivalent Adsorption of the Ions of an Electrolyte

Adsorbent.	Adsorbed Substance,	c_0 (Millimol/Litre) before Adsorption.	c (Millim./L.) after adsorption for	
			Anion.	Kation.
Blood-charcoal[5]	NH_4Cl	102	92·5	93·5
,, ,,	NH_4Br	100·5	84·5	86·2
,, ,,	NH_4CNS	100	60·5	68·4
Kaolin[6]	Methylene blue chloride	5	4·56	0
,,	,, ,, ,,	2·5	2·5	0
,,	Diaminoacridinium chloride	2	2	0
,,	Diaminomethylacridinium chloride	2	1·77	0

It was formerly believed that it was always the ions derived from the water, $H^{\cdot}$ or OH', which neutralized those remaining behind in solution in place of those adsorbed; adsorption would thus be combined with a hydrolytic decomposition of the water. That a *fission adsorption* of this kind only occurs very rarely indeed,[7] if at all, appears from the experiments of Freundlich and Neumann,[8] and most decisively from those of L. Michaelis and Rona.

In almost all cases we find, on the contrary, an *exchange adsorption*: the ion, entering the solution as neutralizing agent, originates in the adsorbent. Either the adsorbent, as we shall have to discuss immediately, is by nature an electrolyte, or it originally contains electrolytes as adsorbed foreign

[1] Ber. d. deutsch. chem. Ges. **21**, 1556 (1888); **22**, 1120 (1889).
[2] Compt. rend. **116**, 517 (1893).
[3] Färberzeitung, 1894/95, p. 119, 188, 286; Chemiker-Zeitung, 1895, p. 426.
[4] Biochem. Zeitschr. **97**, 57 (1919).
[5] *Rona* and *L. Michaelis*, Biochem. Zeitschr. **94**, 240 (1919).
[6] *L. Michaelis* and *Rona*, Biochem. Zeitschr. **97**, 57 (1919).
[7] Perhaps in the adsorption of aniline salts (*Masius, loc. cit.* p. 177).
[8] Zeitschr. f. physik. Chemie, **67**, 538 (1909).

substances, and it is an ion from these which goes into solution. Hence it is generally not $H^{\cdot}$ or OH' ions which we afterwards find in the solution. In the case of exchange adsorption by one group (charcoal, kaolin, and other substances), it is frequently calcium ions,[1] and in the case of another group, exemplified by ferric hydroxide, it is chlorine ions.[2]

An experiment due to L. Michaelis[3] makes the separation of anion and kation in exchange adsorption directly visible. If a drop of methylene blue eosinate is brought on to filter paper, there results a blue circle surrounded by a red margin; the more weakly adsorbed eosin ion has penetrated further with a kation derived from the paper. In adsorption by paper we are dealing with an exchange adsorption of the most decided kind (cf. p. 213). Upon the basis of experimental results so far obtained, we shall in future assume in the case of every non-equivalent adsorption an exchange adsorption, if no especial reasons lead us to think otherwise.

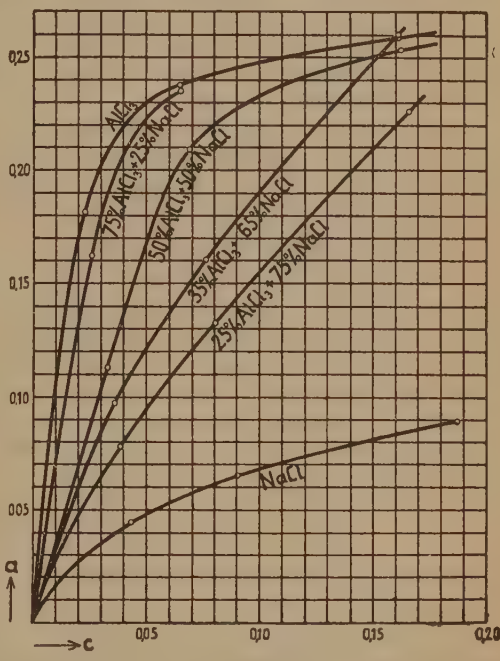


Fig. 40.—Adsorption Isothermals of Solutions of two Salts.

The displacement, too, of one adsorbed substance by another has a distinctly different character when we are dealing with electrolytes. Thus one electrolyte may not only depress the adsorption of another by displacement, but can, under certain circumstances, increase it; or more correctly, the adsorption of an ion may be increased by a second oppositely charged one. Thus NaCl and $AlCl_3$ are taken up by blood-charcoal by equivalent adsorption, but NaCl much more weakly than $AlCl_3$: much less Cl' ion will therefore be adsorbed in a NaCl solution than in an $AlCl_3$ solution equivalent to it in Cl-ion content. If we add $AlCl_3$ to a NaCl solution, much more Cl-ion is taken up in this mixed solution, since the Al'''-ion is abundantly adsorbed and takes an equivalent amount of Cl'-ion with it. Fig. 40, from Rona and Michaelis,[4] shows how with a comparatively small addition of Al'''-ions the adsorption of the Cl'-ion is so increased that it is, in a solution fairly rich in $Na^{\cdot}$-ions, not greatly different from that in a pure $AlCl_3$ solution. In this figure the amount of Cl'-ion adsorbed (in millimols per gram of charcoal) is plotted against the Cl'-ion concentration

[1] *Freundlich* and *Neumann*, *loc. cit.* p. 204; *L. Michaelis* and *Rona*, *loc. cit.* p. 204.
[2] *L. Michaelis* and *Rona*, Biochem. Zeitschr. **97**, 72 *et seq.* (1919).
[3] Pflüger's Archiv. **97**, 634 (1903).
[4] Biochem. Zeitschr. **94**, 250 (1919).

in the solution (mol per litre), and we have either pure solutions of NaCl and $AlCl_3$, or mixtures of the two salts. Since the acids are so much more strongly adsorbed than their salts, an addition of H˙-ion to a salt with the same anion produces a quite extraordinary increase in the adsorption of the anion in question. On the other hand, the addition of alkali to a salt with like kation acts in the same way. Good examples of this behaviour are found in the adsorption of dyes ; the adsorption of acid dyes is strongly increased by acids, that of basic dyes by alkalis.[1]

If, on the other hand, we consider the adsorption of two kations, the anion remaining the same, we find a mutual displacement of kations, and similar rules to those found on p. 199 for the adsorption of non-electrolytes. Thus the strongly adsorbed kations, H˙-ions and multivalent kations, displace univalent kations ; strongly adsorbed anions, OH′-ions and multivalent anions displace univalent anions. While therefore two similarly charged ions mutually displace one another, oppositely charged ions can favour each other's adsorption.[2]

Non-electrolytes also displace electrolytes according to the rules above stated. It would, however, appear, as far as present evidence goes, that this displacement is less than one might expect according to the displacing action of two non-electrolytes upon each other.[3]

The question suggests itself as to how far we are justified in regarding the weak electrolytes, such as the organic acids, as equivalent to non-electrolytes, and how far their dissociation makes itself felt. The results up to date do not show any difference in behaviour as compared with non-electrolytes. The mutual displacement is immediate and pronounced, and according to Rona and von Tóth,[4] the displacement of glucose from blood-charcoal by acetic acid remains the same when the concentration of acetate-ion is greatly increased by addition of sodium acetate, or that of H˙-ion by addition of HCl ; the phenomenon depends therefore upon the adsorption and displacement by the acetic acid itself. This behaviour thus corresponds entirely to that of the fatty acids at an air surface (see p. 73).

Adsorption by Heteropolar Adsorbents

On the basis of these facts we shall certainly follow L. Michaelis and Rona[5] in distinguishing a *polar* from an *apolar* adsorption. As apolar we shall count the adsorption of non-electrolytes and weak electrolytes by various adsorbents as discussed above on pp. 172 to 201, and also the adsorption of strong electrolytes by charcoal, assuming that both ions are taken up in equivalent amount. On the other hand, we are dealing with a polar adsorption when kations and anions of electrolytes are not taken up in equivalent amounts. Adsorption may be exclusively polar, as in the case of kaolin and other substances (see Table 73), when only one kind of ion can

[1] Among others, *Siegrist, loc. cit.* p. 170.

[2] Attention may also be drawn to the measurements of *Estrup* [Kolloidzeitschr. **14,** 8 (1914)] and of *Schilow* and *Lepin* (*loc. cit.* p. 123) on the adsorption by charcoal in mixtures of electrolytes ; the authors named did not succeed, as did *Michaelis* and *Rona*, in clearly defining the conditions.

[3] *Kruyt* and *van Duin*, Kolloidchem. Beihefte **5,** 269 (1914) ; *Rona* and *L. Michaelis*, Biochem. Zeitschr. **94,** 251 *et seq.* (1919). The statement of *L. Michaelis* and *Lachs* [Zeitschr. f. Elektrochem. **17,** 1, 917 (1911)] that non-electrolytes do not displace electrolytes, has not been generally confirmed.

[4] Biochem. Zeitschr. **64,** 290 (1914).

[5] Biochem. Zeitschr. **102,** 268 (1920).

be adsorbed ; it may be partly polar and partly apolar when, as in the case of charcoal, both anions and kations are adsorbed, one in excess in that it displaces by exchange an ion of an impurity found upon the charcoal. In the case of this mixed adsorption on charcoal we have reason to suppose that the apolar adsorption must be ascribed to the charcoal itself, the polar, on the other hand, to the impurities in it. Exchange-adsorption (and possibly also adsorption accompanied by hydrolytic decomposition) are not the only cases of polar adsorption. It is also to be assumed when, for instance, a basic adsorbent takes up an acid. The expression " polar adsorption " is probably better than " electric adsorption " ; the latter might give rise to the idea that in the case of polar adsorption the forces at work are of a different nature from those acting in the case of the apolar variety. This is not the case ; we are most probably dealing, in the case of polar adsorption, simply with the adsorption of heteropolar substances by heteropolar adsorbents. How we are to picture such heteropolar adsorbents (amorphous solid and also crystalline) may first be discussed somewhat more fully.

Silicates are known which have a decided power of taking up the kation of any electrolyte from solution, while returning to the solution a kation which was originally contained in them. I refer to the amorphous permutites first made by Gans,[1] which are prepared by melting together quartz, kaolin, and alkali carbonate, and washing with water. They probably consist of silicates of alumina. We also have the naturally crystalline zeolites of similar composition, and probably also of similar constitution. The beautiful experiments of G. Schulze[2] also prove that this exchange goes forward readily and quickly at room-temperature, and that not only the external surface of the permutite takes part in it, but also the inner surface to a considerable degree. The question may be left open, whether it is advisable to regard this taking-up simply as an adsorption on the inner surface, or as the formation of a solid solution, which would depend, as it were, upon an adsorption upon the surface of the silicate molecules. These substances behave like amorphous solid electrolytes, of which one ion—here the anion—is *sluggish* and forms, as it were, the skeleton, while the mobile kation is able to penetrate the skeleton uniformly. *Adsorbents which adsorb electrolytes polarly are probably also amorphous solid electrolytes of this kind with one sluggish and one mobile ion.* This is not to be taken to mean that they necessarily allow, as do many permutites, the mobile ion to diffuse through in a short time. In many cases this is certainly not inconceivable. It is at present more probable that only the surface of the solid which borders on the solution takes part in this exchange. We need only recall that glass at high temperatures is able to take up ions such as Na, Ag, in thick layers by direct exchange.[3] It is then only natural to suppose that the surface of the glass can quickly exchange the kation at ordinary temperatures, and, in fact, glass powder is able to adsorb electrolytes by exchange.[4]

This is not the only possibility for the creation of such an amorphous heteropolar adsorbent. An originally homopolar adsorbent might also have so strong a tendency to adsorb ions of a certain polarity that these

[1] Jahrb. d. Königl. Preuss. Geolog. Landesanstalt **26,** 179 (1905) ; **27,** 63 (1906).
[2] Zeitschr. f. physik. Chemie, **89,** 168 (1915).
[3] *Heydweiller* and *Kopfermann,* Ann. d. Physik (4), **32,** 739 (1910) ; *G. Schulze, ibid.* (4), **40,** 335 (1913).
[4] *v. Georgievics, loc. cit.* p. 204.

ions, firmly anchored to the interface, might play the part of the sluggish ion, while the oppositely charged ion would behave like the mobile ion; or the adsorbent—say an oxide—might be contaminated by a basic salt, and a polar adsorption be present only as long as the basic salt takes part in it. This is frequently the case according to the experiments of L. Michaelis and Rona.[1] Oxides such as HgO, NiO, ZnO, which are prepared by careful ignition of nitrates, appreciably adsorb acid dyes by exchange, so long as they still contain traces of oxides of nitrogen; if these are removed as carefully as possible, the power of adsorption disappears.

Fundamentally, each ion as an independent substance has its own adsorbability. Since a separation of the ions in appreciable quantities is impossible, the adsorption of a strongly adsorbable kation would have to be accompanied by the adsorption of an equivalent amount of the anion, did not a further possibility exist in the case of the amorphous solid electrolytes; namely, that the strongly adsorbable kation should displace from the surface of the adsorbent an equivalent amount of the mobile kation present there, which enters the solution and neutralizes the amount of anion left behind. Polar adsorption in heteropolar adsorbents would thus come about. In this case it is quite possible that the principal valencies should play a greater part than is generally the case in adsorption. Nevertheless, the difference, also emphasized by Langmuir,[2] is always present as compared with ordinary chemical compounds; in the case of an ordinary chemical compound, one or more molecules of the adsorbent react with all their valencies with the molecules of the adsorbed substance; in the case of adsorption, on the other hand, only with a part. By means of the remainder, the structure of the adsorbent is maintained, whether as space-lattice (in the case of crystalline substances), or in the manner of an internal pressure (in the case of amorphous solids).

Experience up to the present appears to be entirely in agreement with this view. In the first place we have the validity of the adsorption isothermal and dependence upon the same circumstances which influence adsorbability in other cases. Then we have the fact that a non-electrolyte displaces electrolytes less. Obviously, the non-electrolyte is not able to take the place of the one ion, and it could only displace the whole electrolyte if it displaced the anion as well as the kation. If this is not displaceable, being the sluggish component of the amorphous solid electrolyte, non-electrolytes should be strictly unable to displace electrolytes, as Michaelis and Lachs[3] originally believed they had discovered. It should be ascertained whether many silicates, glass, etc., do not belong entirely to this type of adsorbent, and whether in their case the non-electrolytes are not entirely unable to displace electrolytes. If, however, the adsorbent is able to adsorb both ions, and only prefers one to a certain degree, a displacement of both ions by non-electrolytes ought to be possible, as has actually been observed.

In the case, just discussed, of the enhancement of the adsorption of one ion by an oppositely charged one, it is not, on the other hand, a question of polar adsorption. The enhancement must necessarily occur if, in the case of an apolar adsorption, one kation, for example, is more strongly adsorbed than another kation simultaneously present in the solution, and the anion is then attracted to the surface along with the more strongly adsorbed kation.

[1] Biochem. Zeitschr. **97**, 73 *et seq.* (1919).
[2] *loc. cit.* p. 122.
[3] *loc. cit.* p. 206.

The dependence upon the nature of the adsorbent can also be very different from the case of apolar adsorption. In the latter case it is quite possible and common (cf. p. 187) for the attraction exerted by the adsorbent upon the adsorbed substance to be specific to only a small extent compared with the very different affinity of the adsorbed substance for the solvent, and especially for water. For this reason we frequently meet the regularity (referred to on p. 188) of the similar serial order of adsorption for different adsorbents, the validity of Traube's rule, and other points. In the case of polar exchange-adsorption, on the other hand, the specific attraction between adsorbent and adsorbed substance will often overcome other influences. For the determining factor is whether the sluggish ion of the adsorbent is an anion or a kation. If it is an anion, kations will be preferentially or exclusively adsorbed; if a kation, anions: and the greater or smaller affinity of the adsorbed substance for water will only need to be taken into account to a subsidiary extent.

Now the nature of the sluggish ion makes itself felt in the charge on the adsorbent. If the anion is sluggish, the adsorbent is negatively charged; if the kation, positively. The charge, as will be discussed later on, p. 255, is characterized by the direction in which particles of the adsorbent migrate kataphoretically. We thus arrive at a connexion between the sign of the charge on an adsorbent and its adsorbing power. *A polar adsorbent tends to take up that ion which bears a contrary charge to itself.* This is plainly shown by basic and acid aniline dyes, of which the first have an easily adsorbed kation, and the second an easily adsorbed anion. They are well known to be for the most part strongly dissociated, and although many of them are more or less colloidally dissolved, a sufficient number of them are so little different from truly dissolved electrolytes that one may unhesitatingly use them as illustrations; for example, methylene blue as basic, crystal ponceau as acid dye. The opposition between positively and negatively charged adsorbents goes in many cases so far that the positively charged adsorbent can only take up acid dyes, and the negatively charged only basic. Thus, the negative adsorbents bole [1] and kaolin only take up basic dyes, and no acid ones.[2] The positive fibrous alumina, on the other hand, cannot be quoted as a well-defined opposite case (Freundlich and Poser). It indeed adsorbs acid dyes strongly, but some basic dyes even more strongly, and in an order which is to a great extent similar to that on the negative bole (cf. p. 210). Ochres seem to behave similarly.[3] Adsorption of basic dyes by kaolin is strictly by exchange, as appears from Table 73. How matters stand in this respect with the adsorption of basic and acid dyes by fibrous alumina has not yet been investigated; ferric oxide, which is also positive, adsorbs acid dyes by pure exchange (Michaelis and Rona).[4] Charcoal takes up both basic and acid dyes; the adsorption is not strictly equivalent; the departure from equivalence in the sense of an exchange may be referred, as already said, to impurities.[5]

We shall do well not to overdo the idea of pure specificity in the case of polar adsorption. Even in the case of a pure or partial exchange-adsorption we often find a like order in the adsorbability of various substances

[1] An earth, closely similar to kaolin, used in medicine [Trans.].

[2] *Freundlich* and *Poser, loc. cit.* p. 183; *L. Michaelis* and *Rona*, Biochem. Zeitschr. **97**, 57 (1919).

[3] *Bouchonnet*, Bull. Soc. Chim. France, **11**, 454 (1912).

[4] *loc. cit.* p. 204.

[5] Particularly *Freundlich* and *Losev, loc. cit.* p. 182; *Freundlich* and *Neumann, loc. cit.* p. 193; *Michaelis* and *Rona, loc. cit.* p. 201.

by various adsorbents, that is, the rule expressed by equation (2), p. 187. This is a sign that here also the difference in the amount of work which is necessary to bring the adsorbed substance from the surface into the body of the solvent is greater than the different affinity between the adsorbent and the ion of the adsorbed substance taken up. Thus, Freundlich and Losev found the behaviour shown in Table 74 for the adsorption of different dyes by charcoal and some fibres.

TABLE 74

Adsorption by Various Adsorbents. Room Temp.

$$\left(\frac{a_{\text{charcoal}}}{a_{\text{wool}}}\right)_{\text{crystal violet}}{}^{1} = 8{\cdot}19$$

$$\left(\frac{a_{\text{charcoal}}}{a_{\text{wool}}}\right)_{\text{patent blue}} = 9{\cdot}92$$

$$\left(\frac{a_{\text{charcoa}}}{a_{\text{silk}}}\right)_{\text{crystal violet}} = 21{\cdot}1$$

$$\left(\frac{a_{\text{charcoal}}}{a_{\text{silk}}}\right)_{\text{patent blue}} = 26{\cdot}9$$

$$\left(\frac{a_{\text{charcoal}}}{a_{\text{silk}}}\right)_{\text{new fuchsin}} = 23{\cdot}2$$

$$\left(\frac{a_{\text{charcoal}}}{a_{\text{cotton}}}\right)_{\text{crystal violet}} = 156$$

$$\left(\frac{a_{\text{charcoal}}}{a_{\text{cotton}}}\right)_{\text{new fuchsin}} = 155$$

As just remarked, bole and fibrous alumina[2] adsorb a number of basic dyes in like order, which order is the following: chrysoidine > malachite green > auramine > new fuchsin > methylene blue > methyl green.

Here it is important that the two adsorbents carry opposite charges, and that the adsorption in the case of bole is strictly polar, while in the case of fibrous alumina it is only partially so. In the case of charcoal the order is similar; chrysoidine is noticeably strongly adsorbed, methyl green weakly.

Marc[3] points out that this rule is especially evident when we compare the amounts adsorbed at saturation, that is, the maximum adsorption. His results, however, relate mainly to hydrophilic colloids. Tswett[4] uses the different adsorbability of various chlorophyll pigments to separate them, and found for various adsorbents (calcium carbonate, sugar powder, and others) the same serial order.

The amount of polar and apolar adsorption can nevertheless be very different for one and the same adsorbent. Thus in the case of the strictly

[1] How far the parallelism in adsorptive power between charcoal and wool extends is still an open question. According to experiments of *Perold* ("Ueber die Verbindungen der Wolle mit farblosen Aminen und Sauren," Diss., Halle, 1904) the rule just mentioned is fairly valid, if his measurements are compared with those of *Freundlich* (*loc. cit.* p. 172) on charcoal. *v. Georgievics* [*v. Georgievics* and *Pollack*, Ber. Wien. Akad. Wiss. **120**, 479 (1911)] obtained, on the other hand, for the adsorption of acids by wool a decidedly different order. It is probable that wool, as an adsorbent which swells appreciably in water, is seriously altered by acids.

[2] *Freundlich* and *Poser*, *loc. cit.* p. 183.

[3] Zeitschr. f. physik. Chemie, **81**, 641 (1913).

[4] Ber. deutsch. botan. Ges. **24**, 316, 384 (1906).

polar adsorption of methylene blue by kaolin, about 12 grams of kaolin are equivalent to 1 gram of blood-charcoal, the adsorption of which is only partially polar; in the pure apolar adsorption of heptyl alcohol, on the other hand, the adsorption by kaolin is many thousands of times weaker than by charcoal.[1]

The charge on an adsorbent is strongly influenced by the presence of other ions, and the question now arises as to how far there is a parallel change in the adsorptive power. The parallelism to be expected is indeed evident, even though the causal relationship cannot always be clearly seen. Thus many adsorbents become more positive by treatment with acids. The reasons for this will be gone into later; we may have charging by $H^{\cdot}$-ions, or the formation of sluggish kations. We should expect from this that acid dyes would be more freely adsorbed by such a stronger positive adsorbent, and basic less freely. Siegrist[2] actually found that charcoal treated with acids takes up crystal ponceau more strongly than untreated charcoal, and methylene blue more weakly. But since the exchange relationships were not determined in detail analytically, we do not know whether we are dealing with an alteration in the exchange-adsorption caused by the impurities in the charcoal, or whether the apolar charcoal becomes a more polar adsorbent by taking up $H^{\cdot}$-ions preferentially, or, finally, whether it is merely due to the fact previously mentioned that an acid is more strongly adsorbed than its salts. The OH'-ion naturally behaves in the similar but opposite way; it charges negatively; the adsorption of acid dyestuffs should be adversely affected, and that of basic ones favoured. As a matter of fact, according to Siegrist, crystal ponceau is more weakly adsorbed by charcoal treated with alkalis than by untreated charcoal.

Other strongly adsorbable kations and anions of high valency act similarly to $H^{\cdot}$ and OH'.

A question not yet cleared up is whether the influence exerted, for example, by salts with multivalent kations upon the adsorption of iodine by starch, saponarin, etc. (cf. p. 189), can be brought into connexion with these influences, or whether it has another cause. A connexion of this kind is somewhat improbable, if we regard the adsorption of iodine as entirely apolar. Should it, however, be polar, being a matter of polyiodides, which we might imagine being formed with other anions al o, the diminution of the negative charge of the adsorbent by a multivalent kation might favour the adsorption of iodine. Another possibility, however, is that of an adsorption of colloidal iodine, and that the salts act as coagulants and hence favour its precipitation.

Something may be added concerning the adsorption of the salts of heavy metals. In the case of their adsorption by blood-charcoal,[3] which is most likely an equivalent adsorption, it was shown that a kation is in general the more strongly adsorbed the smaller its solution pressure.

The order

$$Ag > Hg > Cu > Pb > Zn$$

[1] *Michaelis* and *Rona*, Biochem. Zeitschr., **102**, 272 (1920).

[2] *loc. cit.* p. 170. For the influence of electrolytes upon the adsorption of dyes, see further *Pelet* and *Grand*, Kolloidzeitschr. **2**, 41, 83 (1907); *Pelet* and *Andersen*, *ibid.* **2**, 210 (1908); *Pelet* and *Siegrist*, *ibid.* **5**, 235 (1909); *Pelet*, Bull. Soc. Vaud. d. scienc. Natur. **45**, 100 *et seq.* (1909).

[3] *H. Morawitz*, *loc. cit.* p. 202.

was found. The smaller the solution pressure of a metallic ion the smaller its tendency to give up an electron, the firmer its attachment by means of the valency electrons to the interface of the adsorbent. Gold chloride is also strongly adsorbed by charcoal. This fact has been employed to demonstrate the presence of the minute amounts of gold in sea water.[1]

Mercuric chloride takes up an exceptional position corresponding to its low dissociation; it is strongly adsorbed by charcoal and other adsorbents, by charcoal about as strongly as butyric acid.[2] The adsorption of mercuric chloride is greatly depressed by the presence of chlorides such as NaCl, $CaCl_2$, and others; the complex anions $HgCl_3'$ and $HgCl_4''$ are therefore much less adsorbed than the pure sublimate.[3] This is noteworthy, since the poisoning effect of the sublimate is also lowered to a corresponding degree by these chlorides. We shall refer to this question later. Zirconyl chloride is also remarkably strongly adsorbed by charcoal.[4]

The Adsorbability of Single Ions

In the case of the adsorption of electrolytes, we can only draw qualitative conclusions concerning the greater or lesser adsorbability of an ion, if—in the case of kations, for example—the adsorption increases or decreases on account of the replacement of one kation by another. A separation of the ions can never occur, and the observed adsorption is always a compromise between the tendency of the more strongly adsorbable ion to go to the interface, and of the more weakly adsorbable one to remain in the solution. The more strongly adsorbable ion will drag the other in part to the interface; the more weakly adsorbable will, on the contrary, partly hold back the more strongly adsorbable in the solution.

In limiting cases we can, however, as Rona and Michaelis[5] have shown, determine numerically the adsorbability of one kind of ion. If a strongly adsorbable ion, say an $H^{\cdot}$-ion, is present in low concentration in a solution, which contains the anion, say Cl'-ion, in great excess, then the amount of Cl'-ion adsorbed is so great that the amount dragged in by the $H^{\cdot}$-ion can be neglected. If the other kation present, say $K^{\cdot}$-ion, is weakly adsorbed, it remains by preference in solution, and the displacement action exerted by it upon the $H^{\cdot}$-ion at the boundary surface of the adsorbent can be neglected as a first approximation. The $H^{\cdot}$-ion can, as it were, move freely; it does not need to drag a Cl'-ion with it, it is not noticeably held back in the solution. Expressed in other terms: if the Cl'-ion is in great excess, then the work required, according to equation (7a), p. 67, to transport it from the surface into the solution, will not be altered by the small amount of HCl added, since the ratio of the concentration in the solution to the amount adsorbed remains practically the same; but this simply means that the adsorption of the $H^{\cdot}$-ion can take place without controlling forces.

Accordingly, we may expect the following:—In a pure dilute (say, 0·01 molar) HCl solution $H^{\cdot}$-ion will be more weakly adsorbed than if we add KCl; with increasing concentration the adsorption of the $H^{\cdot}$-ion reaches a constant maximum limiting value, which is not different from

[1] *Brussow*, Kolloidzeitschr. **5**, 137 (1909); and *particularly H. Koch*, *ibid.* **22**, 1 (1918).
[2] *H. Morawitz*, *loc. cit.* p. 202.
[3] *Rona* and *Michaelis*, Biochem. Zeitschr. **97**, 94 *et seq* (1919).
[4] *Freundlich* and *Kämpfer*, Zeitschr. f. physik. Chemie, **90**, 681 (1915).
[5] Biochem. Zeitschr. **97**, 85 (1919).

that which is obtained say with H_2SO_4 in a K_2SO_4 solution. Now this agrees with actual experiment, in the case of HCl, HNO_3, and H_2SO_4. While, for example, in a pure HCl solution, originally 0·0095 molar, 0·35 millimol per gram of blood-charcoal were adsorbed, this amount already increased in a solution which was about 0·0095 molar for HCl and 1 molar for KCl, to 0·45, and to 0·46 when it was 2 molar for KCl. The values for HNO_3 and H_2SO_4 were only slightly different. A solution which contains about 5 millimol $H^{\cdot}$-ions per litre is therefore in equilibrium with blood-charcoal, upon which about 0·45 millimol per gram are adsorbed.

A similar argument may be given for the OH'-ion, and was proved in a similar manner. The surprising fact emerged, that $H^{\cdot}$- and OH'-ions are about equally adsorbed. It should be remarked that in pure solution OH'-ions are apparently considerably less adsorbed than $H^{\cdot}$-ions; in an originally 0·01 molar KOH solution, 0·27 millimol of OH'-ions were adsorbed per gram of charcoal; but the amount finally increased in a 2-molar KCl solution to 0·47 millimol.

The equally strong adsorbability of $H^{\cdot}$- and OH'-ions on charcoal is the cause that charcoal, provided that it does not contain impurities with a strong tendency to impart a charge, has practically no tendency to take on a characteristic charge in water, which is seen, for example, in the small kataphoretic velocity of carbon particles.

Cellulose and some other Adsorbents: Capillary Analysis

Adsorption on cellulose (filter-paper) is, according to Rona and Michaelis,[1] a pure exchange-adsorption. The apolar adsorption of substances such as heptyl alcohol is extremely small; that of acid and basic dyes, on the other hand, is very distinct. In the case of methylene blue the Cl'-ion remains almost quantitatively in solution, and is neutralized by $Ca^{\cdot\cdot}$-ion from the paper. In the case of the ammonium salt of eosin the $NH_4^{\cdot}$-ion remains in solution. Hence adsorption by paper containing ash is stronger than by ash-free paper. It is therefore the inorganic contaminations, especially calcium silicate, which interact with the dyes by exchange adsorption.

The phenomena appearing in adsorption by cellulose are among the oldest known of their kind.[2] We need only allow the solution of a suitable dye to run out upon ordinary filter paper in order to see that a separation of solute and solvent takes place; in the middle there remains a coloured circle, which is surrounded by a colourless ring of the solvent. That the limit of the coloured circle is so sharply defined depends upon the form of the adsorption isothermal.[3] The steep rise of the amount adsorbed in small concentration results in a comparatively large adsorbed amount corresponding to a very small concentration, i.e. at the edge of the coloured circle.

These experiments are generally conducted by dipping broad strips of filter paper into the solution, and determining the height to which

[1] Biochem. Zeitschr. **103,** 19 (1920).

[2] See particularly *Goppelsroeder*, Verh. Naturf. Ges. in Basel, **14** (1901), and Kolloid-zeitschr. **4,** 23, 94, 191, 236, 312 (1909); **5,** 52, 109, 159, 200, 250, 305 (1909); **6,** 42, 111, 174, 213, 268 (1910); *Skraup*, Wien. Monatshefte **30,** 675, 773 (1909); *Skraup, Krause,* and *v. Bichler, ibid.* **31,** 753 (1910); *Skraup, v. Bichler, Lenz, E. Philippi, Priglinger, ibid.* **31,** 1067 (1910); *Skraup* and *E. Philippi, ibid.* **32,** 353 (1911); *Krulla, Zeitschr. f. physik. Chemie,* **66,** 307 (1909); *Gordon,* J. Phys. Chem. **18,** 337 (1914).

[3] *Krulla, loc. cit.* under [2].

the dissolved substance and the solvent rise. Following Schöenbein,[1] Goppelsroeder[2] worked out this phenomenon on an extensive scale to an analytical method, called *capillary analysis*. It is excellently suited to separate quickly and by simple means complicated mixtures of substances in cases where many other methods fail. It is naturally not confined to coloured substances, since by subsequent moistening with suitable reagents, the zones of the paper may be coloured.[3] The sensitiveness of the method may be very great under suitable circumstances. Goppelsroeder[4] was able, for example, to prove the presence by this means of 0·000000025 mg. of methylene blue in 1 c.c. It is no doubt destined to render valuable service in the case of many physiological and biological questions (detection of certain substances in certain parts of cells and the like), especially as the limit of its refinement is scarcely reached yet. One might use fine threads of paper or other fibres, and employ the microscope for the recognition of the zones of colour.

For numerical calculation, experiments of this kind are hardly suitable, since the amount adsorbed is not in equilibrium with a definite concentration, the former changing, in the case of the drop upon filter paper, for example, in concentric circular rings, which decrease towards the periphery. Besides, it also depends upon the velocity with which the liquid penetrates and rises; this will be discussed later (cf. p. 483). It would therefore carry us too far to consider how the equation found by Holmgren,[5]

$$k = c_0 \frac{r^2 - r_a^2}{r_a^2}$$

in which c_0 is the initial concentration of the solution, r the radius of the liquid circle, r_a that of the coloured circle, k a constant, is to be interpreted.[6]

For the theory of polar adsorption, an exact knowledge of the behaviour of *permutites* and *zeolites* would be of particular importance. In spite of the extensive researches which are available upon this point,[7] it is still difficult to judge how best to regard this phenomenon. In the case of many of these alumino-silicates the exchange of the kations takes place almost quantitatively. Thus, G. Schulze[8] found that sodium permutite, which had lain for one day in a moderately concentrated silver nitrate solution, had exchanged 96·5 per cent. of its sodium (potassium, calcium) for silver.[9] Since the sodium most certainly is not confined to the surface, we must assume that the silver atoms penetrate the whole mass and replace

[1] Verh. d. Naturforscher Ges. i. Basel, III Teil, p. 249 (1861).

[2] *loc. cit.* p. 213.

[3] See also *Grüss*, "Biologie and Kapillaranalyse der Enzyme." Gebr. Börnträger, Berlin, 1912.

[4] Kolloidzeitschr. **4**, 107 (1909).

[5] Biochem. Zeitschr. **14**, 181 (1908); Kolloidzeitschr. **4**, 219 (1909).

[6] See *H. Schmidt*, Kolloidzeitschr. **13**, 146 (1913); **24**, 49 (1919); **26**, 152 (1920).

[7] See among others *Wiegner*, J. f. Landwirtsch. **60**, 111, 197 (1912); Count *Rostworowski* and *Wiegner*, *ibid.* **60**, 223 (1912); *Wiegner*, Zentralbl. f. Mineral. u. Geolog. 1914, 262; *Hissink*, Landwirtsch. Versuchsst. **81**, 377 (1913); *Rob. Gans*, Zentralbl. f. Min. u. Geol. **1913**, 699, 728; **1914**, 273, 299, 365; *Aarnio*, *ibid.* **1914**, 69; *Stramme*, *ibid.* **1914**, 80; Frl. *Zoch*, Chemie d. Erde, **1**, 219 (1915); *Rothmund* and Frl. *Kornfeld*, Zeitschr. f. anorg. u. allgem. Chem. **103**, 129 (1918), **108**, 215 (1919), **111**, 76 (1920); *G. Schulze*, Zeitschr. f. Elektrochem. **25**, 330 (1919).

[8] *loc. cit.* p. 207.

[9] For completeness and speed the previous treatment of the zeolites is apparently also of importance; a fresh desmin exchanges bases more completely and quickly than a dried one, according to *Beutell* and *Blaschke* [Zentralbl. f. Min. u. Geol. **1915**, 142].

the sodium atoms of each permutite molecule. We might say that solid solution takes place. But it still appears questionable whether we ought to separate this as something essentially different from adsorption. The forces which hold the solution molecule together are certainly of exactly the same nature as those acting in the case of adsorption, as will be discussed later in dealing with imbibition (cf. p. 671).

The similarity with ordinary polar adsorption is in fact great. The equilibria are frequently set up smoothly and quickly. If we follow the dependence of the amount of a kation taken up upon the concentration of the solution, the adsorption isothermal generally holds to a great extent. Now it is, as Rothmund and Frl. Kornfeld [1] correctly point out, more correct to refer the results not to the concentration of *one* ion, but always to the ratio of the two ions which enter into exchange; since for every ion taken up another enters the solution. Hence both concentrations always change. In this respect the exchange of ions in permutites differs from the apolar adsorption in mixtures, but not from the polar exchange-adsorption; for in the latter case also an ion enters the solution for every one entering the adsorbent. Hence, if we count, as we do here, polar adsorption as an adsorption phenomenon, it is not in this respect different from the exchange of bases in permutites and zeolites. Hence we ought also in the case of exchange-adsorption to refer in the calculation always to the ratio of concentration of the interacting ions.

Rothmund and Frl. Kornfeld regard the exchange of bases in zeolites and permutites as the formation of a solid solution, and deduce from this standpoint for ions of equal valency at complete dissociation the equation

$$\frac{a_1}{a_2} = \phi\left(\frac{c_1}{c_2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here the suffixes 1 and 2 relate to the two ions which enter into exchange. According to this equation the equilibrium is independent of the volume of the solution, and therefore remains unchanged whether liquid be added or evaporated. To a certain extent this relation is valid. It cannot be taken as hostile to the view of a polar adsorption, since it follows immediately in the case of ordinary adsorption if the exponent $\frac{1}{n}$ has the same value for both ions, which is only likely in the case of ions of like valency. The general dependence of the amount taken up upon the concentration is given, according to the two investigators named, by an equation

$$\frac{a_1}{a_2} = \alpha\left(\frac{c_1}{c_2}\right)^{\frac{1}{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which entirely corresponds to the adsorption-isothermal; the exponent has, moreover, the value 0·3 to 0·7.

It is not intended to assert that the exchange of bases in permutites and zeolites is to be regarded throughout as polar adsorption, but only that the grounds for one or other view hitherto put forward do not appear to be decisive. Perhaps a decision would be given by an investigation of kations of quite a different kind, such as those of the organic bases, dyes and the like, and comparison of their behaviour in the case of ordinary exchange-adsorption, and further by the definite demonstration of gaps which may occur in the range of mixtures. The existence of such gaps was

[1] *loc. cit.* p. 214. See also *G. Schulze, loc. cit.* pp. 207 and 214.

surmised by Rothmund and Kornfeld in the taking-up of thallium and calcium by sodium permutite.

The question whether this exchange of bases should be regarded as polar adsorption or not is influenced by the fact that zeolites are also able to exhibit strong apolar adsorption.[1] Zeolites, such as chabazite and gmelinite, are able, when their water has been removed by heating, to take up quickly and reversibly gases such as ammonia, vapours such as iodine, mercury, alcohols, whereby the optical properties are partly changed and pleochroism is brought about. G. Schulze[2] describes along with the exchange of bases an adsorption, set up comparatively slowly, of salts in aqueous solution by many permutites. An investigation of their behaviour towards gases and solutions, and a further comparison with the behaviour of charcoal under similar conditions, should do a great deal to elucidate the connexion between apolar and polar adsorption.

If finally the interpretation as adsorption should be preferred, we should have, since the exchange is practically quantitative, an adsorption on the molecules of the permutite. This appears quite possible on account of its rigid skeleton.

It cannot be adduced in favour of adsorption that the external physical properties of the zeolites and permutites change comparatively little upon exchange of bases taking place. This curious property is met with in the case of many silicon compounds, even when the chemical composition in the ordinary sense is greatly changed. Thus Kautsky[3] found that, by treatment with hydrochloric acid, calcium silicide, Si_2Ca, may be converted through a series of strongly reducing solid intermediate compounds (unsaturated silicon compounds of the empirical composition Si_2OH_2 and $Si_2O_2H_2$) to silicic acid without change in the external form of the crystalline Si_2Ca leaflets. These substances also have an easily accessible open framework. This is shown by the speed with which chemical reactions pass through the solid mass, and by the power of strongly adsorbing dissolved substances, so that they are coloured by dyes uniformly throughout the entire mass.

It follows from what has been said that we cannot at present distinguish the exchange of bases by zeolites and permutites from exchange-adsorption. When in the following pages we speak of one or the other they will be regarded as similar. It is well known that tilled soil possesses the capacity for this exchange of bases in the highest degree. It depends partly upon a content of zeolite-like silicates, partly upon the so-called humus substances, which, amorphous and gel-like, contain sluggish anions and mobile kations. To the adsorbents of this kind belong moss-peat of the moors, and the fresh peat-moss, sphagnum, from which it has been formed. Although these adsorbents are not definite, Baumann and Gully[4] have collected such a large amount of experience concerning them that they may be shortly dealt with here. Moss-peat and peat-moss give an acid reaction upon direct contact with test-paper, but they do not appreciably give up acid to water. This is a phenomenon often met with in the case of adsorbents with sluggish anions.

[1] *Friedel*, Bull. d. l. soc. franç. d. Min. **19,** 263 (1896); **21,** 5 (1898); **22,** 5 (1899); *Grandjean*, Compt. rend. **149,** 866 (1909); Bull. d. l. soc. franç. d. Min. **33,** 5 (1910).

[2] *loc. cit.* p. 214.

[3] Zeitschr. f. anorg. u. allgem. Chem. **117,** 209 (1921).

[4] Mitt. d. K. Bayr. Moorkulturanstalt, Heft 4, p. 31 (1910). The criticism of *Tacke and Süchting* [Landwirtsch. Jahrb. **41,** 717 (1911)] and others is only justified in certain details [see further *Gully*, Mitt. d. K. Bayr. Moorkulturanstalt, Heft 5, p. 85 (1913), and *Aarnio*, Geol. Kommiss. i. Finland Geotekniske Meddelanden, Nr. 16 (1915)].

They are naturally charged negatively. Accordingly they adsorb mainly kations from salt solutions, and give up to the solution in exchange H'-ions and other kations.[1] The adsorption isothermal is largely followed. In not too concentrated solutions, uni- and bivalent kations are adsorbed in equimolecular concentrations about equally when the anion is the same. The quantity of kation adsorbed depends upon the nature of the anion present in the solution; it increases in the order

$$\text{Cl, Br, } NO_3 < SO_4 < \text{acetate}^{2}$$

Whether the result depends more upon the strength of the acid or upon the lyotropic series has still to be decided.

Here, as in the case of many other polar adsorbents, we must remember that preliminary treatment with solution of electrolyte, particularly acid, can bring about changes, which are not easy to explain *a priori*. It is by no means the case, as is the rule with amphoteric substances such as the proteins (to be treated of later), that we simply have a positive charging-up of the adsorbent. It is more likely that other adsorbed kations, which depress the negative charge of the adsorbent, can be washed out, and the negative charge thereby increased; it may also be that the acids actually open up the adsorbent, and increase the content of sluggish ions and hence the charge. Thus Harris[3] describes the phenomenon that a kaolin which did not show strong exchange-adsorption adsorbed much more strongly by exchange after treatment with acid and subsequent washing.

While charcoal is the adsorbent of greatest power it is also the example of an apolar adsorbent; not, however, as we have often pointed out, a pure one, since we observe to a greater or less degree, especially in the case of dyes, an exchange. Nevertheless, apolar adsorption appears to preponderate as a rule, as is decidedly evidenced by the fact that electrolytes are adsorbed equivalently to a great extent. We may conclude from the apolar adsorption that it is actually carbon which causes adsorption, and not the impurities; it is from these that the small amount of polar adsorption is derived. In favour of this view we have further the circumstance that gas-adsorption on charcoal, which is necessarily apolar on account of the non-electrolytic nature of gases, goes largely parallel to that in solutions; that is to say, if we compare different preparations of charcoal, to which one must ascribe different specific surface areas and greater or lesser amounts of contained impurity, the adsorptive power for gases runs parallel to that in solutions. Thus H. Fischer[4] found that a series of charcoal preparations, partly of technical and partly of laboratory origin, not only adsorbed gaseous SO_2, C_2H_4, and CO_2, but also succinic acid, iodine and methylene blue from aqueous solution, in the following order:

" Spezialkohle " > animal blood-charcoal > " Superiorkohle " > " Karbonkohle " > walnut charcoal > hornbeam charcoal

This parallelism may be occasionally completely masked by the velocity of adsorption being very different. It is not enough simply to wait sufficiently

[1] *Deveaux* [Compt. rend. **162**, 561 (1916)] describes a taking-up with exchange of kations by the cell-texture of plants (also living ones) which is probably to be interpreted as an adsorption.

[2] *Masius* (*loc. cit.* p. 177) found that in adsorption of aniline salts on charcoal aniline is more weakly adsorbed from the HCl solution than from the acetic acid.

[3] Biochem. Zeitschr. **64**, 289–290 (1914).

[4] From unpublished work.

long for final equilibrium to be set up. The structure of the charcoal may be so dense that an adsorbed substance with large molecules does not reach at all a large part of the internal surface on account of the fineness of the numerous pores, which are fully effective in the adsorption of a substance with small molecules. Since gases generally have smaller molecules than many solutes, the departure from parallelism goes entirely in the direction that very dense charcoals, such as cocoanut, adsorb more freely in gases than in solution. For dissolved substances it comes after "Karbonkohle" in the above series, while a very porous wood-charcoal from the firm of Friedr. Bayer & Co., Leverkusen, comes in front of it and after animal charcoal. In the case of gases, on the other hand, cocoanut charcoal and walnut charcoal (also very dense) move up in front of the Bayer charcoal. How great the influence of adsorption velocity may be appears from the fact that with cocoanut charcoal and aqueous solutions of succinic acid equilibrium is only reached after many hours, whereas with gaseous CO_2 it is reached in a few minutes; and if we test the adsorptive power, as is frequently the custom in technical work, by shaking for a few minutes with methylene blue solution, the cocoanut charcoal has apparently a much less adsorptive power in solution, since the large methylene blue molecule is not able to reach the internal surface even after a long period of time.

For many technical purposes, for example for use as gas-filters, the velocity of adsorption is just as important, if not more so, than adsorptive power—by which we understand, as always, the amount taken up when equilibrium is reached—and the rapid adsorption by the very porous charcoal of Bayer is of particular advantage.

That in the comparison of these charcoals the adsorption exponents $\frac{1}{n}$ (for the same substance) were not quite equal, as we should require, according to Mecklenburg,[1] if the adsorbent were really the same in these cases (namely, pure carbon), arises from the fact that the impurities in the carbon have also to be taken into account for the adsorption, as they appear in the partially polar adsorption of methylene blue.

If we relinquish the demand for a high adsorption velocity, the method mentioned earlier (see p. 134) for making a good gas-adsorption charcoal should also give a charcoal active in solution. Th. Graham[2] already found that dried blood ignited in potash gives a charcoal which adsorbs powerfully in solution, while without potash only inactive preparations are obtained. In agreement with this a similar process enables a good gas-adsorption charcoal to be obtained by heating wood and other materials with potash, but not when, other things being equal, the potash is omitted. As already mentioned, the action of the potash probably depends upon the decomposition of tarry compounds, which act partly by coating the surface of the carbon and partly by hindering access to parts of its internal surface.

Adsorption on Crystalline Surfaces

Up to the present we have been dealing almost exclusively with adsorption upon amorphous solids. In the few cases in which adsorption upon crystalline solids was touched upon (cf. p. 182) it did not differ from ordinary adsorption. Now certain facts are known which appear to be

[1] *loc. cit.* p. 186. [2] *loc. cit.* p. 134.

characteristic of crystalline adsorbents. Marc [1] believes that the conclusion may be drawn *that crystals as a rule adsorb such truly dissolved substances as are isomorphous with themselves.* The experiments in support of this rule do not relate to truly *isomorphous* substances, but to *homoiomorphous* ones. These have a very similar crystalline form and hence can crystallize together in parallel overgrowths, while they can scarcely form solid solutions with one another, and do not mutually act as nuclei in cases of supersaturation. Thus Chile saltpetre, and not ordinary saltpetre, is homoiomorphous with rhombohedral calc-spar, while on the other hand ordinary saltpetre and not Chile saltpetre is homoiomorphous with hexagonal aragonite, and also with barium carbonate, with which aragonite is isomorphous. Powdered calc-spar did, in fact, take up Chile saltpetre appreciably, but not ordinary saltpetre, while, on the other hand, finely powdered barium carbonate took up potassium saltpetre distinctly more strongly than sodium saltpetre.

Such behaviour is quite probable. Isomorphous (or homoiomorphous) atoms and atomic groups can replace atoms and atomic groups of the adsorbent at the extreme limits of the space-lattice, and will do it to such an extent as to give the minimum of free surface energy. It is probable that in the case of adsorption of this kind the same regularities hold as in other cases of adsorption. We can apply throughout considerations similar to those advanced by Langmuir (cf. p. 130).

We might further expect that the adsorption of a substance at the different crystal faces of one and the same adsorbent would be of different strength. In the case of the adsorption of dyes by crystals results are available which tell in favour of this ; but it is preferable to discuss these phenomena later (cf. p. 336) in connexion with velocity of crystallization and the influence upon it of foreign substances.

A few remarks may be added concerning the adsorption, investigated by Marc, of dyes and colloidally dissolved substances such as albumin, dextrin, and starch by crystalline adsorbents such as uric acid, $BaSO_4$, $SrCO_3$, $BaCO_3$, and $PbCO_3$. The most important results have already been anticipated. The adsorption isothermal is to a great extent applicable ; a marked saturation is reached, often at fairly low concentrations [2] ; if we compare the amounts adsorbed at saturation, the order of adsorption is the same for different adsorbents. This discovery fits well into the general theory of adsorption. It was not mentioned earlier that here again an influence of the charge of the adsorbent is unmistakable. We can clearly distinguish two groups : one, to which gypsum and $MgCO_3$ belong, adsorbs practically only basic dyes, and is therefore negatively charged ; the other, in which are, for example, sulphates and carbonates of strontium, barium, and lead, takes up practically exclusively acid dyes, and is therefore positively charged. There are also some which, like charcoal and fibrous alumina (see p. 209) adsorb both basic and acid dyes. Obviously we must also take account of the charge in the case of crystalline adsorbents, and hence of the difference between polar and apolar adsorption.

[1] Zeitschr. f. physik. Chemie, **75**, 710 (1911) ; **81**, 641 (1913).

[2] *Marc* points out that saturation in the case of many adsorbents and adsorbed substances is reached gradually and continuously as the concentration increases ; while in the case of others it appears as if a sharp bend exists in the isothermal. It is not impossible that in the latter case the adsorbed substance undergoes a chemical change at the surface.

Adsorption of Radio-Elements

The adsorption of radio-elements must be considered separately, since these substances occur in quantities millions of times smaller than those hitherto considered. In these quantities they do not appreciably alter the interfacial tension, since the adsorbed atoms or molecules, as the case may be, only come into the surface-layer in scattered single units. We have to go back directly to the attractive molecular forces in order to explain this adsorption.

The idea which might at first suggest itself, that no strict regularities can be found on account of the exceedingly small concentration, is not at all confirmed. On the contrary, the investigations of Paneth and Horowitz [1] brought to light the following rule. *A radio-element is strongly adsorbed by a difficultly soluble heteropolar adsorbent—salt or oxide—when it would also form a difficultly soluble compound if it were present in greater amount.* Thus radium is strongly adsorbed by $BaSO_4$ and $BaCrO_4$, because $RaSO_4$ and $RaCrO_4$ are difficultly soluble, while it is not adsorbed by AgCl and Cr_2O_3, because $RaCl_2$ and RaO are easily soluble. Thorium B, which belongs to the lead pleiad, is adsorbed when the corresponding lead compounds are difficultly soluble; thorium C, which belongs to the bismuth pleiad, when the corresponding bismuth compounds are difficultly soluble.

The concentration of the radio-elements in question was in these experiments much too small for the solubility product with the ions in solution to be reached. It could also be shown that the effect did not depend upon the nature of the anions present in the solution, but upon the anion of the difficultly soluble adsorbent.

The following explanation, given by Paneth,[2] is very illuminating. If we consider the solubility equilibrium kinetically, then from the difficultly soluble $BaSO_4$, $Ba^{\cdot\cdot}$- and $SO_4^{\prime\prime}$-ions will continually be passing into solution, or depositing themselves on the solid substance. If thorium B ions are also present in the solution, they will also arrive at the boundary surface of the adsorbent. Since they tend to give with $SO_4^{\prime\prime}$-ions difficultly soluble Th-B sulphate, the probability is great that they will unite with the SO_4 atomic groups of the adsorbent in the solid system in the same manner as Ba atoms would do. The number of Th-B atoms retained and thus also their adsorption is consequently great. If, on the other hand, Th-C ions are in solution and arrive at the boundary surface, the probability that they will be held back is much smaller; they will rather tend, on account of the greater solubility of Th-C sulphate, to go into solution with $SO_4^{\prime\prime}$-ions.

Upon an adsorption of this kind depends, as Paneth points out, the phenomenon observed by Fajans and Beer,[3] that a radio-element is carried down by a difficultly soluble precipitate when it would itself give a difficultly soluble precipitate under the conditions of the experiment, supposing it were present in greater quantity.

The purest case of this kind of substitution of one atom for another is isomorphism. That isomorphism and homoiomorphism are favourable to adsorption upon heteropolar crystalline adsorbents, was found by Marc

[1] Zeitsch. f. physik. Chemie, **89,** 513 (1915); Sitzungsber. Wien. Akad. Wiss. **123,** 1819 (1914).

[2] Phys. Zeitschr. **15,** 924 (1914).

[3] Ber. d. deutsch. chem. Ges. **46,** 3486 (1913); further *Fajans* and *F. Richter, ibid.* **48,** 700 (1915).

(p. 219, above). With the loose nature of the attachment which distinguishes adsorption, it is extremely probable that at the boundary surface other atoms also bring about saturation, in so far as they are able to yield a difficultly soluble compound similar to the adsorbent. It would be of importance to test whether, in the case of adsorption by isomorphous adsorbents as investigated by Marc, the condition of difficult solubility plays a part or not. The adsorption of the radio-elements belongs, as we see, entirely to polar adsorption. The close connexion between slight tendency to solution of the adsorbed substance and adsorbability in the case of apolar adsorption of active substances is known (cf. p. 199).

Since the number of the atoms of radio-elements in such experiments is mostly very small and far from sufficient to cover the surface-layer to an appreciable extent, we may assume that the numbers of atoms adsorbed is simply proportional to the number of collisions between them and the adsorbent, and hence proportional to their concentration in the solution. The ordinary adsorption isothermal is not therefore valid, but the simple law of Henry holds, as has appeared already in the adsorption of gases at very low pressures, and on occasion also in the case of adsorption in solutions (cf. p. 191). As a matter of fact, Ritzel [1] found that when uranium X_1 was taken up by blood-charcoal in aqueous solution containing uranyl nitrate, the radio-element distributed itself between adsorbent and solution according to Henry's law.

How far this taking-up of uranium X_1 by charcoal is a polar adsorption has not yet been completely cleared up, and the same applies to the cases investigated by Paneth and mentioned above. In any case, along with the adsorption other processes take place. At first a rapid change of concentration occurs, as we should expect for an adsorption, but it is some ten days before equilibrium has been reached. In the case of a pure adsorption a much more rapid attainment of equilibrium is to be expected. Presumably we must suppose with Ritzel that the UX_1 is at first adsorbed upon the surface, but then diffuses into the interior of the adsorbent; a sorption, therefore, probably similar to that discussed above, on p. 215, in the case of permutite. Whether in the phenomena investigated by Paneth a diffusion into the interior of the adsorbent follows upon adsorption requires closer investigation.

Ritzel [2] found in the taking-up of UX_1 by blood-charcoal the curious phenomenon that thorium salts have a great power of depressing this sorption, and even of stopping it; 0·00039 millimols of $Th(NO_3)_4$ per litre suffice to depress the amount of UX_1 taken up by about 20 per cent., 4 millimols per litre to completely prevent it.[3] This may be explained as follows: Th is isotopic with UX_1, and it will therefore saturate the valencies of the adsorbent in the same way, and be able to diffuse into the interior. Since it is present in much greater amount than UX_1, it will displace the latter, as in the case of permutites a kation present in greater concentration displaces that present in a smaller.

Now quite other materials can displace the UX_1 from the charcoal, substances that are by no means isotopes, but are only in general strongly

[1] Zeitschr. f. physik. Chemie, **67**, 724 (1909). On the other hand, *Berry* [J. Chem. Soc. **97**, 196 (1910)] found for the adsorption of UX_1 in uranyl nitrate solution by freshly precipitated $BaSO_4$ the ordinary isothermal.

[2] Zeitschr. f. physik. Chemie, **67**, 747–748 (1909).

[3] *Freundlich* and *Kaempfer*, Zeitschr. f. physik. Chemie, **90**, 684 (1915).

adsorbed; for example, benzoic acid, strychnine nitrate, methylene blue, chrysoidine, zirconyl chloride, and others.[1] With these, however, the phenomenon is not reversible; they only displace when they reach the charcoal simultaneously with, or in advance of, the UX_1, but not if they are added subsequently. In the case of thorium salts, on the other hand, even when they are added last, the UX_1 is displaced from the charcoal in accordance with the existence of true equilibrium. The "false" equilibria with other foreign substances are apparently to be interpreted in the same way as the action, to be discussed later, of foreign substances upon crystallization from supersaturated solution (cf. p. 338). They largely occupy the interface, since they are present in so much greater quantity, and hence greatly diminish the probability that UX_1 atoms should be taken up there and be able to diffuse into the interior. Since they themselves are unable to penetrate into the interior to any extent, they are not in a position to displace UX_1 when it has once penetrated, while Th, which also penetrates, can do so.

In the case of these other foreign substances the active concentrations are also very small; with benzoic acid, a concentration of 0·006 millimol per litre gives an increase in the UX_1 concentration in the solution of about 10 per cent. But if we remember that with a concentration of 0·006 millimol in solution about 0·2 millimol of benzoic acid corresponds to a gram of charcoal, and that along with it only about 8×10^{-9} millimols of UX_1 are present in the charcoal, so that there are about 10^8 times more molecules of benzoic acid on the charcoal than atoms of UX_1, the action observed is not surprising.

The displacing action which easily adsorbable substances exercise upon UX_1, together with its easily measured radio-activity, may be used to measure the adsorption of substances whose content is not easily determined directly.

We may add that other, non-radio-active substances in very small concentrations are displaced by other adsorbable substances from the surface of charcoal according to entirely the same laws as UX_1; this was proved, for example, for the displacement of copper-ions by $Th(NO_3)_4$.[2]

In this kind of adsorption, most probably apolar, as observed here for charcoal, the relationship to slight solubility is not so evident as in the cases observed by Paneth; it has to be taken into account in other cases involving the radio-elements. Thus UX_1, which like thorium is soluble in a solution of ammonium carbonate, is nevertheless adsorbed in such solution by a hydroxide, provided that Th salts are absent. If these are present in the solution, the UX_1 does not go to the ferric hydroxide, since it is displaced from it by the Th present in excess in precisely the same way as was the case for charcoal.[3]

Ebler[4] points out that the adsorption of the radio-elements may be usefully employed to separate them from other substances and to prepare them pure; as an adsorbent which is effective and easily removed, he recommends silicic acid gel.

[1] *Freundlich, W. Neumann,* and *Kaempfer,* Phys. Zeitschr. **15,** 537 (1914); *Freundlich* and *Kaempfer,* Zeitschr. f. physik. Chemie, **90,** 681 (1915).

[2] *Freundlich, Neumann,* and *Kaempfer, loc. cit.* under [1].

[3] Verbal communication from Prof. *O. Hahn.*

[4] *Ebler* and *Fellner,* Ber. d. deutsch. chem. Ges. **44,** 2332 (1911); Zeitschr. f. anorg. Chemie, **73,** 1 (1911).

The Influence of Temperature upon Adsorption in Solution

The dependence upon temperature of adsorption at the interface solid—liquid is strongly reminiscent of that at the interface solid—gas, as Figs. 41A and B show (the c values are again mol per litre, the a values millimol per

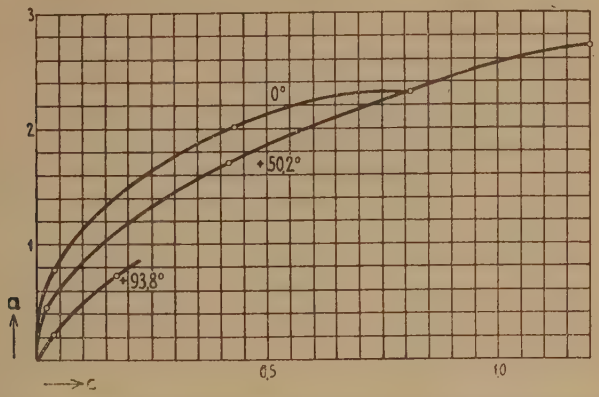


Fig. 41A.—Adsorption Isothermals of Solutions at different Temperatures.

gram of charcoal). The experimental results available are not very numerous. Only for acetic acid in aqueous solution on blood-charcoal, to which Figs. 41 A and B refer, are series of experiments at fairly widely separated temperatures available.[1] As we see from the $\log_{10}a$, $\log_{10}c$ graph

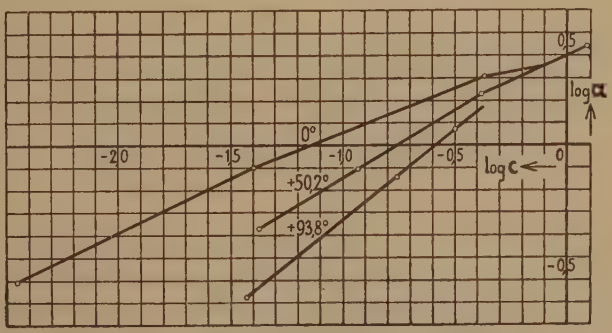


Fig. 41B.—Adsorption Isothermals of Solutions at different Temperatures, plotted logarithmically.

(Fig. 41B), the ordinary isothermal holds for all temperatures, and the adsorption exponent $\frac{1}{n}$ changes in a manner similar to that of the adsorption

[1] *Freundlich*, Zeitschr. f. physik. Chemie, **57**, 446 *et seq.* (1907); further, *B. Schulz*, "Ueber die Adsorption in Lösungen," Diss., Königsberg, 1908, p. 15 *et seq.* (experiments in aqueous solutions of acetic acid and iodine with charcoal as adsorbent); *Freundlich* and *Bjercke*, *loc. cit.* p. 175.

of gases by charcoal (see p. 114, and Figs. 22 A and B). Table 73, indeed, shows that the isobars also may be calculated from a formula

$$\log_{10} a_t = \log_{10} a_0 - (\zeta - \xi \log_{10} c)\, t. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The isobar relates to a $c = 0{\cdot}1$ mol per litre. Everything else that was said on p. 117 concerning the dependence of adsorption on temperature may be applied unaltered to the present case. The agreement would be

TABLE 75

Influence of Temperature upon the Adsorption of Acetic Acid by Blood-charcoal in Aqueous Solution

$\zeta = 0{\cdot}00055$; $\xi = 0{\cdot}00395$

t.	a (obs).	a (calc.).
0°	1·15	1·17
50·2°	0·73	0·70
93·8°	0·47	0·44

still greater, and would extend to an equal order of magnitude for ζ, if the adsorption of gases were referred not to pressures in centimetres of mercury, but to concentrations in mol per litre ; the ζ of Table 43 then assumes a value of about 0·0002 (instead of about 0·015) as against 0·00055 in Table 75. From further experiments of this kind the further conclusion may be drawn that the dependence upon temperature is usually small.[1]

As opposed to adsorption of gases, but in agreement with adsorption at the interface between two liquids (cf .p. 94), an increase of the adsorption with increase of temperature may also occur. Such a case was found by Pelet and Grand in the adsorption of methylene blue by charcoal and silicic acid in aqueous solution ; that by charcoal is partly polar, that by silicic acid entirely so. The similarity to the dependence on temperature described for acetic acid is in so far retained, as here also $\frac{1}{n}$ increases with rise of temperature ; $\xi = \frac{d\frac{1}{n}}{dt}$ remains positive (cf. p. 118). Now, in the equation (1), just mentioned, the expression $\xi \log_{10} c$ preponderates to such an extent over the ζ that a positive amount is added to $\log_{10} a_0$. These results of Pelet and Grand[2] were confirmed by Siegrist[3] for the adsorption of methylene blue and crystal ponceau on charcoal. The latter's observation is new, that in this adsorption of electrolytes the charge on the adsorbent also comes into play in the dependence upon temperature. If the charge favours the adsorption of the strongly adsorbable ion—a positive charging by acids, therefore, in adsorption of crystal ponceau—the ordinary isothermal remains valid over a wide range of concentration even at high temperatures.

[1] See, for example, the adsorption of phenylthiourea in aqueous solution [*Freundlich* and *Bjercke*, Zeitschr. f. physik. Chemie, **91**, 11 *et seq.* (1916)].

[2] Kolloidzeitschr. **2**, 4 (1907).

[3] "Contribution à l'étude des phénomènes d'adsorption." Diss., Lausanne, 1910, p. 25 *et seq.*

If, on the other hand, the charge is inimical to adsorption—positive charging in the adsorption of methylene blue—the adsorption curve at high temperatures already shows at low concentrations a course corresponding to the general adsorption curve ; that is, a maximum and subsequent decline.

With what other properties the magnitude and sign of the temperature coefficients are connected has not yet been determined.

It would certainly be worth while to make a comparative investigation of the temperature coefficients of the adsorption of a substance and its tendency to dissolve—solubility or partition coefficient between two liquids—and to test whether similar relations hold to those discussed on p. 76 for the dependence of the surface tension of solutions on temperature and for the solubility of the dissolved substance in question. In the case of dissociated substances, as Pelet and N. Andersen [1] point out, changes in the degree of dissociation and in the nature of the ions with temperature are certainly also of importance for the dependence on temperature.

The *heat of adsorption* of dissolved substances is difficult to measure, and very exact calorimetric measurements would be necessary for its determination. It appears as a very small difference between two large heat-changes, the heat of wetting with the pure solvent and with the solution. Gore [2] has made experiments with silicic acid and other adsorbents and aqueous solutions of electrolytes, in which, however, only changes of temperature, and not amounts of heat, were determined. Kruyt and van der Spek [3] found a positive heat-change when they allowed moist charcoal, the further heat of wetting of which could most probably be neglected, to adsorb crystal violet from aqueous solution ; about 16 gram-calories were developed in the adsorption of about 2 millimol of crystal violet by 5 grams of blood-charcoal.

Adsorption in Solutions and Chemical Processes

Upon this subject the same may be said as was put forward on p. 139 concerning the adsorption of gases and chemical processes. We can again distinguish *direct* and *indirect* actions of adsorption.

A case of direct displacement of chemical equilibrium by adsorption is not known. Such cases possibly occur occasionally with polar adsorption, although experience hitherto supports the view that it is exclusively a question of exchange adsorption. That is to say, when after adsorption from a solution of a neutral salt the solution has an acid reaction, it is more probable that $H^{\cdot}$-ions already present on the adsorbent were forced back into the solution, than that by displacement of equilibrium the more strongly adsorbable base was formed and adsorbed in larger amount. Such examples are perhaps met with in the case of the adsorption of aniline salts (cf. p. 204). This question still awaits final elucidation.

The great number of cases in which reaction velocities in solution are influenced by adsorption depend upon indirect actions. We can again distinguish between inhibited and non-inhibited adsorption catalysis.

Non-inhibited Adsorption Catalysis

A case in which it could be very clearly proved that the magnitude of a catalytic action is proportional to the amount of an active substance

[1] *loc. cit.* p. 211. [2] Phil. Mag. (5), **37**, 306 (1894).
[3] Kolloidzeitschr. **24**, 152 (1919).

adsorbed, was found by v. Elissafoff [1] in the decomposition of hydrogen peroxide by glass wool in the presence of the salts of heavy metals. It is well known that the decomposition of H_2O_2 is accelerated both by glass alone and also by salts of Mn, Cu, etc. If now we allow glass wool and heavy metal salts to act together, the decomposition proceeds much more quickly than corresponds to a purely additive effect; thus, for example, the decomposition (in arbitrary units) with 0·5 gram of glass wool in 20 c.c. of a 12-millimolar H_2O_2 solution was 0·86; under the same conditions, but without glass wool and with addition of $CuSO_4$ in 1·54 millimolar concentration, the decomposition was 1:63; with the same copper concentration plus 0·5 gram of glass wool, 10·8.

It is *a priori* probable that the decomposition of the H_2O_2 takes place on the surface of the glass, and that the Cu adsorbed, which is much greater in amount per unit of volume there than in the solution, causes the great acceleration. This was well confirmed by the following fact. The velocities of decomposition, which could be approximately calculated as unimolecular reactions, had, for two copper concentrations of 1 and 10 millimol per litre, values of 0·0013 and 0·0023 respectively, being therefore in the ratio 1 : 1·77. The amounts of copper adsorbed at the same concentrations were 0·0022 and 0·0038 millimol per gram of glass powder (of the same Jena glass as the wool); the ratio is 1 : 1·73. The rate of decomposition is thus obviously proportional to the amount of Cu adsorbed; it is this which interacts with the H_2O_2 adsorbed on the glass.

In the curious decomposition of formic acid by rhodium according to the equation

$$HCOOH = H_2 + CO_2,$$

which was thoroughly investigated by Blackadder,[2] we follow the velocity of a chemical reaction. In favour of this view we have the slight influence of the velocity of stirring, the temperature coefficient of about 2 - a fact which is, however, not absolutely conclusive (cf. p. 150)—and also the order of the reaction. The dependence, namely, of the velocity upon the concentration c of the formic acid may be well represented by an equation

$$-\frac{dc}{dt} = kc^{\frac{1}{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which integrated gives

$$k = \frac{1}{\left(1 - \frac{1}{n}\right)t}\left(c_0^{1-\frac{1}{n}} - c^{1-\frac{1}{n}}\right).$$

Exactly as in the case of the decomposition of SbH_3 (cf. p. 140), this must be valid when only the adsorbed part of the formic acid reacts. But we are not dealing here, as in the case of SbH_3, with a simple decomposition, but with an interaction with an unknown compound of rhodium containing oxygen or sulphur; for one of the two latter substances must be present if rhodium is to decompose formic acid; and during the process some H_2S is always developed when sulphur is present. That the reaction goes best in weakly acid solution, and hence is favoured by addition of sodium formate, depends upon the fact that H'-ions are disadvantageous, perhaps on account of a reaction with this Rh compound. Na formate does not increase the

[1] Zeitschr. f. Elektrochemie, **21**, 352 (1915).
[2] Zeitschr. f. physik. Chemie, **81**, 385 (1912).

adsorption of the formic acid, as one might suppose. Blackadder was able to show this directly, and it is also not to be expected in view of the results of Rona and v. Tóth (no change in adsorption of acetic acid by acetate or hydrochloric acid, cf. p. 206). In alkaline solution no decomposition takes place; this probably depends upon the fact that the salts of organic acids are much more weakly adsorbed than the acids themselves (cf. p. 203). As we see, a characteristic optimum of velocity of decomposition in weakly acid solution is thus brought about.

A further example of a similar kind, in which the adsorbed portion of the reacting substance is transformed, is the reaction between sodium hypophosphite and water investigated by Sieverts and Peters,[1] which takes place on platinum black according to the equation

$$NaH_2PO_2 + H_2O = NaH_2PO_3 + H_2.$$

Here again the dependence upon the hypophosphite concentration is given by the differential equation (1). Here again the slight influence of stirring speed, and the temperature coefficient = 2, show that we are dealing with a chemical process. The velocity increases, as we should also expect, proportionately to the surface of the Pt black, hence for one and the same preparation proportionately to the amount of it present.

In solution also we must often reckon with the displacement pointed out by Reichinstein (cf. p. 145). The examples discussed by him stand in close relation to electrode processes, so that they will be better dealt with later (cf. p. 305).

The many reactions investigated only qualitatively, in which an adsorption catalysis is present, will not be discussed here. Attention may merely be drawn to certain processes, in which the adsorbent itself takes part in the reaction. In the adsorption of gold chloride by charcoal, there is not only an exchange; the gold is found as metal in the charcoal. Avery[2] assumes that a reaction takes place according to the equation

$$4AuCl_3 + 6H_2O + 3C = 4Au + 12HCl + 3CO_2.$$

To me it seems more probable that the exchange adsorption leads at first to the formation of a compound between Au and a silicate ion or an organic ion (or even to formation of gold hydroxide), which is then easily reduced by the charcoal by a similar reaction. Other salts of noble metals—for example, silver nitrate and acetate—behave similarly under suitable experimental conditions. These phenomena have in part been known for a very long time[3] and have attained technical importance.

Further and in part similar reactions are observed in the adsorption of dichromate ions by various adsorbents. With fibrous alumina as adsorbent[4] we only notice that upon shaking with a solution of potassium dichromate the orange colour changes to the yellow of the chromate, which is most simply explained by supposing that the OH'-ion enters the solution by exchange adsorption and there forms with Cr_2O_7''-ions CrO_4''-ions. When blood-charcoal is the adsorbent a similar exchange-adsorption seems to take place at first, entailing the same transformation. In this case it was further shown by Oryng[5] that CrO_4''-ions are far less adsorbed than Cr_2O_7''-

[1] Zeitschr. f. physik. Chemie, **91,** 199 (1916).
[2] J. Soc. Chem. Ind. **27,** 255 (1908).
[3] *Th. Graham,* Pogg. Ann. **19,** 143 (1830).
[4] *Ishizaka,* Zeitschr. f. physik. Chemie, **83,** 105 (1913).
[5] Kolloidzeitschr. **13,** 9 (1913).

ions. But the adsorption is followed, as Oryng showed, by a further chemical reaction, which leads to the formation of $Cr^{\cdots}$ ions in solution and probably of $Cr(OH)_3$ upon the adsorbent.

Permanganate ions are also strongly adsorbed by blood-charcoal with exchange, and reduced by a subsequent reaction.[1]

Inhibited Adsorption Catalysis

A case of inhibited adsorption catalysis is known in which apparently the one reacting substance inhibits its own oxidation by forming an adsorption layer; this was only a probable assumption for the oxidation of CO on quartz-glass (cf. p. 151). We refer to the oxidation, measured by O. Warburg,[2] of oxalic acid by oxygen upon blood-charcoal, according to the equation

$$2(COOH)_2 + O_2 = 4CO_2 + 2H_2O.$$

Of the substances appearing in this equation, the oxalic acid is by far the most strongly adsorbed. Hence it forms a layer upon the charcoal, through which the oxygen must first diffuse in order to react quickly with it upon the surface of the charcoal. We start, as on p. 147, from the differential equation

$$-\frac{d(O_2)}{dt} = \varkappa \cdot D \cdot \omega \frac{(O_2)_1 - (O_2)_0}{\delta}$$

$\varkappa$, D, ω, and δ have the same significance as before, but D is the diffusion constant of the oxygen; $(O_2)_1$ is the concentration of the oxygen in the adsorption layer at the interface of the latter with the solution, $(O_2)_0$ that at the surface of the charcoal. If the change in the amount of oxygen is expressed in terms of the corresponding change in the oxalic acid concentration c, and if we take into account that $(O_2)_1$ is constant, and that $(O_2)_0$ can be put equal to zero, we finally get the differential equation

$$-\frac{dc}{dt} = k' \frac{1}{c^{\frac{1}{n}}},$$

which, integrated, gives

$$k = \frac{1}{t}\left\{c_0^{1+\frac{1}{n}} - c^{1+\frac{1}{n}}\right\}.$$

Here k and k' are constants, $\frac{1}{n}$ the adsorption exponent. The measurements agree with this formula to a great extent, even with a considerable change in the initial concentration of the oxalic acid.

Further, O. Warburg was able to prove that urethanes sensibly inhibit the reaction. This may be explained by their taking a large part in the formation of the adsorption layer on account of their adsorption, hence altering the thickness of the layer. The inhibition[3] by the urethanes should be proportioned to the amount adsorbed, and hence must depend, according

[1] *Oryng*, *ibid.* **11**, 169 (1912).

[2] Pflüger's Archiv, **155**, 547 (1914); the results in part calculated by *Freundlich* and *Bjercke*, Zeitschr. f. physik. Chemie, **91**, 31 *et seq.* (1916).

[3] It was measured relatively: if v_0 was the volume of O_2 which disappeared in two hours in the absence of urethane, v that in the presence of urethane, then

$$H = 100\,\frac{v_0 - v}{v_0} \text{ is the inhibition.}$$

to the adsorption isothermal, upon the concentration in the solution. This was the case.[1]

One would further expect that the inhibition would increase as we ascend the homologous series of the urethanes according to Traube's rule. This was also the case, and the increased inhibition corresponded numerically with the increased amounts adsorbed. With an initial concentration of the urethane of 0·3162 mol per litre, the following values were obtained for the inhibition H :

TABLE 76

Inhibition of the Oxidation of Oxalic Acid on Charcoal by Urethanes. $c_0 = 0{\cdot}3162$ Mol per Litre. $t = 38°$

Substance.	H.	q = Ratio of H Values.
Methyl urethane	41·88	
Ethyl urethane	58·75	$\frac{H_{ethyl}}{H_{methyl}} = 1{\cdot}40$
Propyl urethane	87·70	$\frac{H_{propyl}}{H_{ethyl}} = 1{\cdot}49$

Compare this with Table 67 on p. 196.

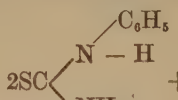
The other possibility still exists, that the inhibition due to urethanes, and to foreign substances generally, depends upon a displacement of the oxalic acid from the places upon the adsorbent at which the oxidation takes place, as is the case with the oxidation of the amino-acids on charcoal to be discussed later (cf. p. 231). Then the chemical reaction at the interface would no longer be very rapid compared with the diffusion. Only a comparison of the course of the reaction in presence and in absence of inhibitory substances could permit of a decision between the two possibilities.

The testing of a reaction with regard to its susceptibility to urethanes and other capillary-active substances and with regard to the applicability of Traube's rule, which may then be inferred, constitutes a useful means of deciding whether a reaction takes place at an interface. O. Warburg has frequently made use of this device with success. Respiration, fermentation, and assimilation were inhibited by urethanes according to Traube's rule, a sign that we are dealing in these cases with interface reactions. Of these, assimilation is particularly sensitive to capillary-active substances, and this is probably the reason why it only takes place with uninjured chlorophyll grains. In the case of assimilation it was also shown that the inhibition depends according to an adsorption isothermal upon the urethane concentration (cf. p. 766).

The case just discussed belongs to a first sub-group, in which *a reacting substance* initially present is concerned in the formation of the diffusion layer, and hence in the inhibition of the diffusion, whilst the final products, CO_2 and H_2O, have no importance in this respect. In a second sub-group the limiting case is the reverse of this ; it is the *end products* which are respon-

[1] The test was not rigorous, since the equilibrium concentrations were not determined, but we may here assume that they were only slightly different from the initial ones.

sible for the diffusion layer and for the inhibition, and the initial substances play no part in comparison with them. In the gas space we had the example of this kind discussed on p. 147 in the formation of SO_3 from SO_2 and O_2 on platinum. Similar to this, according to Freundlich and Bjercke [1] is the oxidation of phenylthiourea by oxygen in aqueous solution on blood charcoal.[2] It proceeds according to the equation



$$2SC(N(C_6H_5)-H)(NH_2) + O_2 = \text{Hector's base}^3 + S.$$

The strongly adsorbable phenylthiourea is always in excess on the charcoal. Its concentration, therefore, is of no account (cf. p. 147), but only that of the oxygen diffusing towards it. Let it again be assumed that the chemical process on the surface takes place rapidly as compared with the diffusion. The final products sulphur and Hector's base are very difficultly soluble in water; they remain therefore almost completely at the interface, and it is likely that they inhibit the diffusion of the O_2 much more strongly than the phenylthiourea also present.

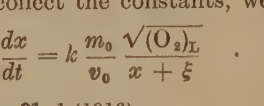
We therefore again start from the differential equation (5), p. 147, but now the thickness of the diffusion layer δ is proportional to the amount of the end-products x contained on the unit of charcoal surface. $(O_2)_l$, the concentration of the O_2 in the diffusion layer, is equal to the product of solubility and concentration in the solution, L. $(O_2)_L$ (cf. p. 147), assuming that the O_2 in the whole layer is likewise present in the form of molecules. But according to our experience up to the present, it would seem as if here also, as is frequently the case, a decomposition into atoms takes place in the layer, so that $(O_2)_l$ will be proportional to the square root of the concentration in the solution. $(O_2)_0$ is again zero. If in the differential equation (5) we express the vanishingly small amount of O_2 by the quantity of end-products which are formed, and also the quantities ω and δ in a corresponding manner, and collect the constants, we get the equation

$$\frac{dx}{dt} = k \frac{m_0}{v_0} \frac{\sqrt{(O_2)_L}}{x + \xi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)^4$$

[1] Zeitschr. f. physik. Chemie, **91**, 1 (1916).

[2] The course of the reaction was followed by a different method from that employed by *Warburg* for the oxidation of oxalic acid. The latter kept everything—even the oxalic acid concentration in the solution—constant, and measured the decrease in the O_2 volume. *Freundlich* and *Bjercke* determined the continuously decreasing concentration of phenylthiourea by titration, keeping the ratio of charcoal to volume of liquid $\frac{m_0}{v_0}$ constant (m_0 being the initial amount of charcoal, and v_0 the initial volume) The change in O_2 concentration was so small that it could be taken as constant.

[3] That this substance



is actually formed in the first instance, could hitherto only be rendered probable.

[4] In the experiments, charcoal was shaken with phenylthiourea solution, so that adsorption first took place, and the considerable decrease in concentration which then followed was ascribed to the chemical reaction. From the phenylthiourea content *after* adsorption x was calculated; ξ is the amount of phenylthiourea which is oxidized while the adsorption is proceeding.

which integrated gives

$$k = \frac{v_0}{2m_0 t} \frac{(x+\xi)^2}{\sqrt{(O_2)_L}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This equation was satisfied to a large extent by the actual experiments.

The temperature coefficient was sensibly greater than one would expect for a diffusion, namely 2·3 between 25° and 35°. This is not necessarily in contradiction with the view just put forward, as has already been shown on p. 150, for in the differential equation (5) the diffusion constant D is not alone influenced by temperature ; a number of other quantities are as well. It is therefore not necessary that the small temperature coefficient of pure diffusion should be found. The latter is only then to be expected in adsorption catalysis, when the diffusion layer is not seriously changed by initial and final products of the reaction, as, for example, in many cases of the catalytic *decomposition* of H_2O_2 on solid surfaces such as platinum (cf. p. 489).

The mechanism of the oxidation of cystine and other amino-acids upon charcoal investigated by O. Warburg and Negelein [1] is, on the other hand, essentially different. These are almost certainly non-inhibited catalytic processes, and not inhibited ones ; for the reaction obviously proceeds proportionally to the first power of the cystine concentration and takes place with practically the same velocity, when further cystine is brought into contact with charcoal which has already oxidized cystine. The absence of inhibition is here comprehensible since both the initial substance, cystine, and also the detectable end-products, CO_2, NH_3, and H_2SO_4, are only weakly adsorbed. Judgment of the type of reaction is, however, rendered more difficult by the circumstance that the oxidation to these final products is apparently not complete. The amount of the oxidation products and the amount of oxygen taken up are only a fraction of the quantity which should be formed or taken up for complete oxidation ; and the yield of oxidation product increases with increasing oxygen pressure and rise of temperature. Perhaps we measure the velocity of a reaction taking place between cystine and oxygen in the adsorption volume. That the cystine concentration enters into the equation to the first power may then be due to the adsorption exponent in its isothermal being perhaps practically equal to unity, as is frequently the case for weakly adsorbed substances at low concentrations.

Here also Warburg found a considerable inhibition due to the presence of other capillary-active substances. It could be shown that this action was due to a displacement of the cystine by the other substances ; they were equally effective, when they took possession of an equal amount of the adsorption surface. Warburg compared the amounts of capillary-active substances, which raised the concentration of the cystine from 0·54 millimol per litre (in equilibrium with 0·05 millimol per gram of charcoal) to 1·1 millimol per litre (in equilibrium with 0·021 millimol per gram of charcoal). The amounts of inhibitory substances adsorbed, the values of a in Table 77, lie very close together, even when we compare the concentrations c in the solution, with which they are in equilibrium. The agreement becomes still better when the surfaces occupied by them are taken into account. Warburg is not satisfied with calculating the surface of a cube containing

[1] Biochem. Zeitschr. **113,** 257 (1921), and *O. Warburg*, Festschr. d. Kaiser Wilhelm-Ges. p. 224 (1921) ; Biochem. Zeitschr. **119,** 134 (1921).

TABLE 77

Inhibition of the Oxidation of Cystine on Charcoal by Capillary-active Substances

Substance.	c Mol per Litre.	a (Millimol per g. Charcoal).	$\frac{n^2-1}{n^2+2} \cdot Mv$.	ωa.
Amyl alcohol (from fermentation)	0·0015	0·87	26·7	7·9
Acetone	0·073	1·33	16·2	8·3
Methylphenylketone	<0·00035	0·73	36·3	8·0
Acetamide	0·17	1·2	14·9	7·3
Valeramide	0·003	0·62	28·7	6·9
Acetonitril	0·2	1·5	11·1	7·7
Isovaleronitril	0·0015	0·83	25·1	7·1
Asym. dimethylurea	0·03	1·1	23·3	9·0
Sym. diethylurea	0·002	0·68	32·4	6·9
Phenylurea	0·0002	0·76	37·8	8·6

1 gram of adsorbed substance $(Mv)^{\frac{2}{3}}$, from the molecular volume Mv, and multiplying this by a, but takes a surface which is proportional to the true one occupied by the molecules; it is proportional, according to the theory of Clausius and Mosotti, to

$$\left(\frac{n^2-1}{n^2+2} Mv\right)^{\frac{2}{3}}.$$

Actually, the surface taken up by a mols adsorbed

$$\omega_a = a\left[\frac{n^2-1}{n^2+2} Mv\right]^{\frac{2}{3}}$$

is more nearly a constant than the expression $a(Mv)^{\frac{2}{3}}$. Here also we naturally have the rapid rise in the homologous series, and the strong capillary activity of the phenyl group. The experiments are particularly illuminating when we assume only one layer of molecules as adsorption layer, in accordance with Langmuir's theory (cf. p. 130).

It is highly probable that this oxidizing action on charcoal does not take place upon the carbon surface itself, but only at places where certain foreign substances are present. In favour of this we have the fact that hydrocyanic acid, which is only weakly adsorbed [1] and hence only displaces feebly, nevertheless inhibits much more strongly than the substances given in Table 77; it already causes in a concentration of about 0·1 millimolar an inhibition which it ought only to exert at about 1 molar concentration judged by its capillary activity. Now, according to what will be explained later (cf. p. 766), we must ascribe this action of hydrocyanic acid to its forming loose complexes with heavy metals present in the charcoal in small amounts, which metals constitute the actual points of oxidation; it thus saturates their residual valencies which come into play in oxidation. Iron is probably the metal which chiefly comes into question [2]; we may recollect the action of iron in the oxidation of charcoal itself by oxygen (cf. p. 143). The whole mechanism

[1] According to measurements by *O. Warburg* [Biochem. Zeitschr. **119**, 160 *et seq.* (1921)] blood-charcoal adsorbs about 0·1 millimol of hydrocyanic acid per gram from aqueous solution at a concentration of 0·01 molar.

[2] *O Warburg*, Pflüger's Archiv, **155**, 558 (1914).

of the cystine oxidation is therefore similar to that described by v. Elissafoff [1] for the catalysis of hydrogen peroxide by small quantities of metal upon glass surfaces. Obviously, such a catalysis by metallic salts at a surface is not opposed to the fact that substances which do not react specifically with the heavy metals inhibit the oxidation simply according to their displacing power.

The Theory of Adsorption

We will first, by way of summary, discuss how far the view of adsorption as a condensation upon a boundary surface has proved of value.

At the interfaces liquid—gas and liquid—liquid, at which the surface tension can be measured, everything speaks in favour of it. We can observe a positive, sensible adsorption of the solute, when the interfacial tension is strongly lowered by it. The experiments of Patrick (cf. p. 91) appear to afford the most convincing proof of this. The taking-up by mercury drops of very different kinds of solutes from water runs throughout parallel with the lowering in the interfacial tension of mercury caused by these substances. It has not so far been possible to determine in this case the numerical connexion between the lowering of interfacial tension and adsorption. This is due to the fact that the determination of the amount adsorbed at the interface is insufficiently accurate.

Does adsorption in solution by solid adsorbents correspond to a condensation on the interface, and is it similar to adsorption on the interfaces before mentioned, and the surface phenomena observed at them? This also may be affirmed unreservedly. Let us take only a few striking surface-tension phenomena in aqueous solution:

The contrast between the very slightly surface-active salts and the much more active acids and bases, and the particularly active organic substances (acids, ethers, esters).

Traube's rule for the homologous series of active substances.

The slight difference in capillary activity of the three chloro-acetic acids.

Point for point we find the corresponding behaviour in the adsorption of these substances by charcoal and other adsorbents (cf. p. 195). Further, the adsorption isothermal follows exactly the course we should expect from the σ, c curve of capillary-active substances, and is exactly similar to the dependence of the amount adsorbed upon the concentration in Patrick's experiments on mercury drops.

It is further in agreement with the above that the absolute amounts adsorbed from the solution are of the same order of magnitude as those condensed by capillary-active substances upon the interface liquid—gas. On account of the difficulty in determining the inner surface of most adsorbents investigated, only a few measurements of the absolute amount adsorbed are available. Bancelin [2] has made a few measurements of this kind with glass lamellæ as adsorbent and dyes (not further specified) in aqueous solution, and found an amount adsorbed of about 10^{-7} gram per sq. cm. For the adsorption of nonoic acid at the interface aqueous solution—air, Donnan and Barker (cf. p. 74) found $1{\cdot}5 \times 10^{-7}$ gram. The comparison is not, however, decisive, since in the case of glass we have polar adsorption, at the interface solution—air an apolar adsorption.

Along with this conception of the matter, depending upon the interfacial tension, the direct attraction of the gases or solvents and solutes by the

[1] *loc. cit.* p. 226. [2] Compt. rend. **158**, 791 (1914).

molecules of the adsorbents has been invoked by way of explanation. The two views do not contradict each other, but differ only in that in the case of the interfacial tension a thermodynamic function is used, while with the attractive force we go back to a molecular-kinetic conception. Both points of view have well-known advantages and disadvantages; the thermodynamic is trustworthy, the molecular-kinetic leads in favourable cases much further and gives a more detailed picture.

If adsorption is interpreted as attraction, it is clearly seen that a specific interaction between adsorbent and adsorbed substance must necessarily be present. And this is actually the case, for example, in the particularly weak adsorption of neon and helium (cf. p. 120), in the influence of the constitution upon the adsorptive power of organic adsorbents for iodine (cf. p. 189), in the relation between the adsorbability of heavy metal kations and their position in the electrochemical series (cf. p. 211), and in many other cases. It should be expressly stated that we must on no account believe that the thermodynamic point of view cannot explain the specific behaviour; for, of course, it makes no preliminary assumption concerning the numerical values of the interfacial tension at a given temperature, nor concerning the values of the coefficients which reproduce the dependence of the interfacial tension upon the concentration; these may have quite specific values. From the standpoint of attractive force we reach the relation between adsorbability and condensability for gases, between adsorbability and tendency to dissolve in solutions, we establish the probable form of the adsorption isothermal, the validity of Henry's law at low pressures and small concentrations, etc. If we so often meet with behaviour but slightly specific, such as the validity of Traube's rule at the interface liquid—gas and on very diverse adsorbents, this is to be explained from the standpoint in question by the attraction between the adsorbent and the various adsorbed substances being not very specific; while the attraction between adsorbed substance and solvent, that is, the work necessary to remove the substance from the surface to the interior of the solvent, is very variable.

What is now the nature of this attractive force? As frequently pointed out (cf. p. 122), this attractive force, and in general the "molecular forces," are to be referred, following Haber and others, to effects of chemical valency, and in the last resort, therefore, to electrical forces. Many are inclined to regard "adsorption compounds" as allied to Werner's compounds, and to separate both more sharply from compounds in which chemical valency in the old sense comes into play. It appears to me altogether artificial to separate Werner's compounds from organic ones,[1] while adsorption com-

[1] In my opinion, to take only one example, there is no fundamental difference between a reaction such as the transformation of purpureo chromic-chloride into roseo-chromic chloride in aqueous solution,

$$[Cr(NH_3)_5Cl]^{\cdot\cdot} + 2Cl' + H_2O = [Cr(NH_3)_5(H_2O)]^{\cdot\cdot\cdot} + 3Cl',$$

and an organic reaction such as the transformation of ε-chloramylamine into piperidine hydrochloride in aqueous solution,

$$ClH_2C(CH_2)_3CH_2NH_2 = \left[\begin{array}{c} H_2C \quad CH_2 \\ H_2C \quad\quad NH_2 \\ C \quad C \\ H_2 \quad H_2 \end{array}\right] + Cl'.$$

In both cases Cl passes by a slow reaction from the internal sphere of action into the external. The chemistry of *Werner's* salts and organic chemistry are distinguished by the fact that a large number of intermediate equilibria are possible between substances slowly transforming themselves.

pounds appear to me to be much looser ; in their case a much larger number of molecules can replace one another. This does not imply that there are no transitions between Werner's and the adsorption compounds.

That certain difficulties have to be overcome, especially in Polanyi's adsorption theory, if we are to refer the adsorptive force to electrically interpreted valencies, was already pointed out above (p. 129). Langmuir's theory, on the other hand, would not meet with any objection in this respect (cf. p. 130).

Michaelis and Rona [1] wish to explain the unusual adsorptive power of charcoal by the position of carbon in the periodic system ; it is just as strongly electro-positive as electro-negative, and therefore tends, instead of putting main valencies into action, to allow its chemical affinity to act by subsidiary valencies. Another circumstance appears to me to be hardly less important. Carbon is the only one of a group of elements (silicon, zirconium, thorium, boron) having oxidation products, CO and CO_2, which are gaseous and comparatively weakly adsorbed. If it should be generally confirmed, as is perhaps already certain for silicon, that these other elements in the finest state of division adsorb weakly (zirconium, for example, can be obtained in a soot-like form [2]), this might be due to the fact that, being easily oxidizable, they adsorb their solid oxidation products and then lose their strongly adsorbing surface.

Here the further question arises, as to whether it is essential for adsorption that one substance, the adsorbent, should enter into interaction with a large number of its molecules, the other, the substance adsorbed, with a smaller number, or whether on occasion it may be useful to designate the interaction between two single molecules as adsorption. Is it part of the essence of adsorption, and is adsorption thereby to be defined, that an adsorbent, as remarked on p. 122, binds the adsorbed substance only with a residue of its valency forces, while the main part of these forces is employed in maintaining the structure of the adsorbent ? An experiment by Barger, [3] that certainly ought to be extended, tells in favour of this view, and of the adsorbent necessarily consisting of a large number of molecules. Saponarin, one of the substances which adsorb iodine with a blue colour, has a true solubility in water at 18° of about 1 part in 7,100. In this concentration and in still smaller ones it is never coloured blue by iodine. The blue colour only appears when the concentration has become so great that the saponarin can separate in the solid form. The blue colour disappears suddenly when the saponarin is again brought into solution by addition of water. One might conclude from this that the molecules of saponarin give no blue colour with iodine, and hence do not adsorb it. In order that an adsorption may take place, larger particles must be present.

This might depend upon the kinetic energy of a complex of one molecule of saponarin + one molecule of iodine sufficing to bring about a dissociation. Although the kinetic energy of the complex (saponarin-granule + several iodine molecules) has the same mean value, it does not suffice to dissociate off simultaneously all iodine molecules. Adsorption would then be favoured by coarse particles, but the presence of such particles would not be absolutely indispensable to its occurrence.

As a matter of fact the assumptions just made are unnecessary when

[1] Biochem. Zeitschr. **97,** 77 (1919).
[2] See *Wedekind,* Lieb. Ann. **395,** 183 (1913).
[3] *Barger* and *Miss Field,* Journ. Chem. Soc. **101,** 1397 (1912).

the molecules of the adsorbent lie in the rigid framework of a solid body, which is of such open build that other molecules as well are able to pass through it. In that case we shall at once be able to regard the interaction between the molecules of the solid and those of the second substance which permeate its structure as adsorption. Examples of this sort were given above (cf. p. 214) in the case of permutites and zeolites. We meet them later in the case of imbibition, and there is at present no good reason for distinguishing these cases from adsorption.

Worthy of note are further the cases in which one can plainly distinguish the adsorption compound from the chemical compound in the ordinary sense, although the distinction is not so sharp where (as frequently in exchange adsorption) we also reckon as adsorption those cases in which the main valencies are at work. Bayliss[1] describes the following experiment. The acid of Congo red readily gives a blue colloidal solution. If this is shaken with freshly precipitated aluminium hydroxide suspended in water, *blue flakes* are first formed, the adsorption compound of hydroxide and the Congo acid; only gradually, particularly on warming, do the flakes become red, and the aluminium salt of the Congo-acid, a chemical compound, is formed. Still more unmistakable is an experiment of Gilbert.[2] Copper hydroxide takes up the acid of eosin in ethereal solution according to the adsorption isothermal; an adsorption compound of continuously variable composition is therefore formed. Under suitable experimental conditions the crystals of copper eosinate can be formed from the amorphous adsorption compound, and have the required stoichiometric composition. A further example found by Thiele[3] is important on account of its relation to the process of dyeing: *p*-nitrobenzylideneaminoguanidine, coloured yellow in solution, colours wool yellow at first; on warming, however, the wool becomes colourless, since its acid groups cause the formation of the colourless salt of the substance mentioned. Ammonia sets the base free again and produces the yellow colour afresh. R. Haller[4] describes a series of adsorption compounds between basic dyes easily soluble in water, such as brilliant green, methylene blue, and others, and difficultly soluble acid dyes such as paranitraniline red, alizarine yellow, etc., in the case of which one might have expected compounds in stoichiometrical proportions. An experiment by Willstätter[5] must likewise be mentioned here, which also shows that we may not regard a polar or exchange adsorption as equivalent to salt formation without further question. The salts of alkaloids are adsorbed by wool by exchange; the alkaloid goes to the fibres, the anion remains for the most part behind in the solution with other kations (H·-ions, etc.). As the wool is optically active, we should expect in the event of pure, salt-like combination that it would on adsorption select an active component from a racemic alkaloid solution. This is not the case; the inactive alkaloid solution remains inactive after adsorption by wool.

We are readily led to consider whether the law of mass-action cannot be successfully applied to adsorption equilibrium. It appears first of all that the simplest suppositions which one could make for its application do not hold good. If (A) is the concentration of the adsorbent, (B) that of the adsorbed substance in the solution, (C) that of the adsorption compound,

[1] Proc. Roy. Soc. **84,** B, 81 (1911).
[2] J. Phys. Chem. **18,** 586 (1914).
[3] Mentioned by *Wedekind* and *Rheinboldt,* Ber. d. deutsch. Chem. Ges. **47,** 2150 (1914).
[4] Kolloidzeitschr. **22,** 113 (1918); **24,** 56 (1919); **27,** 30 (1920).
[5] Ber. d. deutsch. chem. Ges. **37,** 3758 (1904).

and if m, p, and q are the number of molecules, then according to the law of mass action

$$(A)^m \times (B)^p = \text{Const.} \times (C)^q.$$

Since A and C are solid bodies they must, if they do not mutually dissolve one another, be introduced in constant concentration, hence

$$(B) = \text{Const.},$$

that is, the concentration of the adsorbed substance should be constant in the solution, as long as both solid adsorbent and solid adsorption compound are present in the solid phase. The course of the adsorption isothermal would be as shown on Fig. 42, curve 2. A course of this kind was actually found by Appleyard and Walker [1] when investigating the taking-up of picric acid by solid diphenylamine in aqueous solution; as long as the concentration of the picric acid remained below the value demanded by the equilibrium constants of about 0·060 molar, no picrate was formed; at a concentration of 0·057 the diphenylamine was completely colourless, at a concentration 0·060 brown picrate was formed, and the concentration remained constant at this value (the values observed varied between 0·0594 and 0·0607), while for the mol of diphenylamine in the solid phase 0·0055–0·0702 mol of picric acid were present. That an adsorption takes quite a different course (see Fig. 42, curve 1) does not need emphasis.[2]

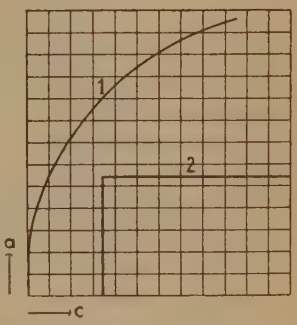


Fig. 42.—Adsorption Isothermals and Equilibrium Curves according to the Law of Mass Action.

In order to arrive at the ordinary adsorption isothermal, the adsorbent or adsorption compound or both have to be regarded as variable phases (solid solutions and the like).[3] If, for the sake of simplicity, we assume the adsorption compound only to be variable, we get

$$(B)^p = \text{Const.}\ (C)^q$$

or

$$(C) = \text{Const.}\ (B)^{\frac{p}{q}} = \text{Const.}\ (B)^{\frac{1}{n}},$$

the equation to the adsorption isothermal when we put $\frac{p}{q} = \frac{1}{n}$. At present no fruitful answer can be given to the questions as to why q is almost always larger than p, and why (within certain limits) $\frac{p}{q}$ differs so little from substance to substance, how its increase with temperature is to be explained, and so on. From Langmuir's considerations (cf. p. 130) it is quite intelligible

[1] *loc. cit.* p. 172.

[2] Concerning cases such as occur, for example, in the taking-up of sodium alizarate and arsenite by Fe_2O_3, where an adsorption isothermal commences, not at the zero of the co-ordinates, but at a definite value of the abscissa, see *W. Biltz* [Ber. d. deutsch. chem. Ges. **38**, 4143 (1905)]; Kolloidzeitschr. **26**, 179 (1920)]; and *Oryng* [Kolloidzeitschr. **22**, 149 (1918)]. It would appear as if an adsorption and a chemical combination, according to main valencies, are superimposed.

[3] *Reychler* [see e.g. J. d. Chim. Phys. **7**, 362 (1909); **8**, 10 (1910); also *W. Biltz, ibid.* **7**, 570 (1909)] attempts to represent adsorption equilibria from the standpoint of the law of mass action.

that both the adsorption compound, in which the adsorbent only partially binds the adsorbed substance with its valencies, and also the adsorbent, may be regarded as variable phases.

Regarding the connexion between adsorption and the formation of solid solutions, the essential points have already been dealt with (p. 109). Final states of equilibrium are obtained at the interfaces liquid—gas and liquid—liquid, in which the dissolved substance has concentrated itself at the interface in virtue of its capillary activity. With adsorption by solid adsorbents these equilibria must also be attained after lapse of sufficient time. But it is important that we are able, according to the experiments of McBain (cf. p. 109), to separate the quickly attained adsorption equilibria from the solution equilibria, which are generally attained slowly. Equilibria which are set up in seconds and minutes may be unhesitatingly regarded as adsorption equilibria, while those which require days and weeks are solution equilibria, or more correctly adsorption + solution equilibria. For we always have along with the quantity taken into the interior the quantity which is condensed on the surface. It has already been frequently stated, however, that it is often difficult to decide by experiment whether we are dealing with an adsorption or a solid solution, and that frequently a distinction appears indeed artificial. This is, for example, the case in the exchange of bases by permutites and zeolites, or in the taking-up of liquids by substances exhibiting imbibition. The equilibria are set up in the case of these solids of open build upon the interior surface also so quickly, that a distinction based upon a greater or lesser speed of adjustment is impossible, and in the equilibrium which is attained, the interior of the solid is quite uniformly permeated by the dissolved substances, as in the case of solid solution. Sometimes the concrete conception of an adsorption leads us farther here than the more formal one of a solid solution. On the other hand, without the need, such as arises in the case of the permutites, to refer the taking-up of the adsorbed substance to an interaction between it and the molecules of the adsorbent, the adsorbent may have so fine-porous a structure that the adjustment of adsorption equilibrium in the ordinary sense takes a very long time. Thus, for example, this may often be the case with cocoanut charcoal and substances of high molecular weight. Experience, however, usually turns out to be simpler than theory, inasmuch as in many cases those adsorption equilibria which are indeed quickly and smoothly reached can be distinguished from solution equilibria slowly attained.

The relation between adsorption at the interfaces liquid—gas and solid—liquid, and the tendency to dissolve in the liquid phases, has already been discussed (cf. p. 70), but not yet the fact that a certain connexion also exists with the tendency to dissolve in the solid phase; this connexion is in the opposite sense to the former. The adsorbability of a dissolved substance is frequently the greater, the less its tendency to solution in the liquid phase, while on occasion it will be the greater, the greater its tendency to solution in the solid adsorbent. For in the case of solution we are unquestionably dealing with the same molecular forces which determine the adsorptive power at the boundary of the adsorbent; if they therefore tend in a high degree to draw the molecules of the solute into the interior of the adsorbent, they must also have a greater tendency to hold it fast on the surface.[1]

[1] This will, however, frequently hold only as long as the partition equilibrium in the interior of the adsorbent is not yet reached. If the solubility there is very great,

Upon this possibly depends the curious connexion between adsorption and partition between two solvents, pointed out by Reinders.[1] The partition of many dyes, such as methylene blue, crystal violet, and others between water and isobutyl-alcohol follows laws quite similar to those for their adsorption by all sorts of adsorbents ; a partition formula

$$c_{\text{alcohol}} = \text{Const.} \times c_{\text{water}}^{\frac{1}{n}},$$

corresponding to the adsorption isothermal, holds ; the exponent is, however, about 0·7, while for the adsorption of these dyes by various adsorbents it is smaller (0·1–0·2) ; bases increase the taking-up of basic dyes by alcohol, acids that of acid dyes, and so forth. Now this behaviour is quite to be expected, as Reinders himself points out. For the dyes in question are polymolecular in water, and monomolecular in alcohol. The partition formula must therefore have the form found. Since, further, the dye-base or dye-acid respectively is more soluble in alcohol than in water, acids and bases must increase the taking-up in the manner observed. In this latter point the real affinity between the two phenomena comes out ; for since the dye-acids and bases are probably more soluble in the adsorbent and less in water than the dye-salts, their greater adsorbability is also explained. The form of the adsorption isothermal cannot be explained in this way. It is, however, also found for adsorption from aqueous solutions of many dissolved substances, which are monomolecular in water. Its form in the case of adsorption is connected with the dependence of the compressibility and volume of the solute upon the concentration, and the mutual displacement of solute and solvent at the surface.

V. Capillary-electrical Phenomena

The term " capillary-electrical " will be used in the following pages in a wider sense than usual. It is to include all phenomena in which electrical changes are associated with changes in the extent and tension of a surface of separation between two phases. A great part of electrochemistry would thus have to be called " capillary-electrical," since the majority of electrochemical processes take place at boundary surfaces. Now, as will be stated more in detail later (cf. p. 297), the electrical conditions at a boundary surface are in many cases, especially for solids in contact with liquids, of such a nature that the capillary influences are without or almost without importance. This is true, for example, of electrode processes in ordinary galvanic cells, as included in Nernst's theory. If, on the other hand, we seek for processes in which capillary influences, such as adsorption, etc., play an unmistakable part, we find especially electro-osmosis, kataphoresis, and the phenomena connected with them, which will be designated here as *electrokinetic*. These ought, therefore, to be considered first, and then the electrical behaviour of the boundary tension of mercury against aqueous solutions and related processes, the group of phenomena hitherto preferentially described as capillary-electric. The properties of the potential change at the boundary surface are less easily comprehended than the electrokinetic processes aforementioned.

only comparatively little may be condensed upon the interface. We have a behaviour like that at the interface of two liquid phases, when the adsorbed substance is very soluble in the organic liquid (see p. 89).

[1] Kolloidzeitschr. **13,** 96 (1913) ; see also *v. Georgievics,* Zeitschr. f. physik. Chemie, **90,** 47 (1916).

(a) The Electrokinetic Phenomena

The electrokinetic phenomena are distinguished by the fact that th displacement of a liquid along a boundary surface (generally solid), c conversely, the displacement of a solid surface relatively to a liquid, produced by an externally applied electromotive force; reversing th process, an E.M.F. may be generated by displacements of a liquid relativel to a solid surface or of a solid surface relatively to a liquid. The followin scheme shows the possible processes of this sort.

A. An external E.M.F. produces motion
   (1) of the liquid against a solid surface: *electrosmosis*;[1]
   (2) of solid particles against a liquid: *kataphoresis.*

B. An externally caused motion produces an E.M.F.
   (1) The liquid is moved relatively to the solid surface: *strean currents*, or more correctly *stream potentials.*
   (2) The solid body is moved relatively to the liquid: *vibratic currents; currents from falling particles*, etc.

For the theory of colloidal solutions the electrokinetic phenomena a of importance, and also for the understanding of the behaviour of mer branes and of other biological processes: they must therefore be treate in detail.

The Physical Laws which condition Electrokinetic Phenomena

Electrosmosis (abbreviated Eo.) will first be dealt with. An experiment arrangement which may be employed to measure it appears in Fig. 43.

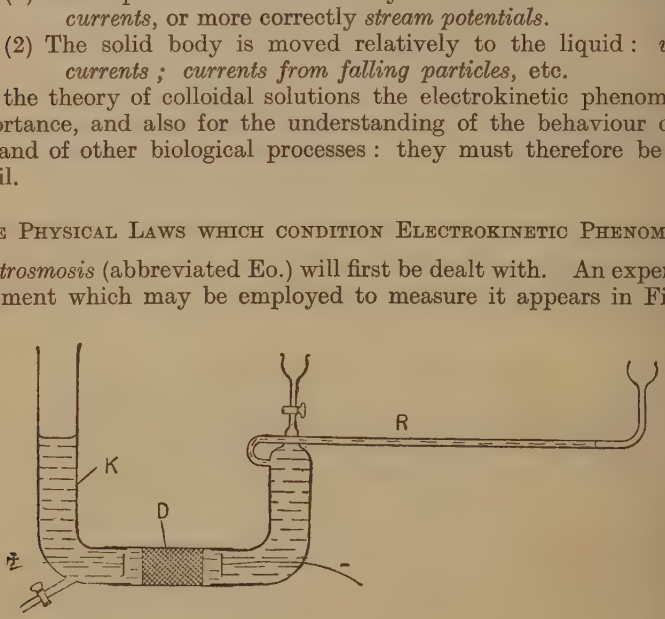


Fig. 43.

D is a system of capillary tubes, say a diaphragm of powdered solid alternatively a single capillary tube, the vessel K being filled with liquid shown. If an E.M.F. be applied in a certain direction to the electrod the liquid commences to rise in the narrow tube R; as soon as a defini level is reached, an equilibrium is set up, which depends upon the electric conditions of the system. If instead of the tube R one with an efflux the side is fused on, the liquid commences to drop out upon the applic tion of the current; according to the electrical conditions a certain amou of liquid will be driven over in a certain time.

This arrangement has the drawback that it does not easily permit different liquids being compared, since it is difficult to restore the diaphrag

[1] The author uses this contracted form originated by v. Smoluchowski. "Electr osmose" has acquired a technological sense, and "electroendosmosis" is mer unnecessarily long. [Trans.]

to its original state by washing it out. In order to meet this, v. Elissafoff [1] made use of a capillary which was set between two electrodes, but separated from them by a small air-space. The capillary was partly filled at one end with the liquid to be investigated. If an electric current flowed in the correct direction through the liquid in the capillary, it moved along the walls and collected at the other end to a drop, the growth of which permitted the measurement of the amount of liquid transferred in unit time. The capillary could be easily cleaned and investigated under comparable conditions. The defect of this arrangement consisted in the necessity of using high potentials, that is, a static machine, and, further, in the electrical conditions not being precisely defined.

Electrosmosis was already observed by Reuss.[2] Wiedemann[3] and Quincke[4] were the first to investigate it more thoroughly; Helmholtz[5] interpreted it quantitatively. His theory was altered later by Lamb,[6] v. Smoluchowski,[7] Perrin,[8] and others, without the final results being seriously changed. The following argument follows Perrin.

Let a cylindrical capillary of radius r be introduced between the electrodes, and let the stationary state have been reached, in which the volume v of liquid is transferred in unit time. Differences in hydrostatic pressure should not be present. The motion of the liquid is regarded as being produced as follows:—The inner wall of the capillary in contact with the liquid is coated with an electrical double layer. We will assume with Perrin that the one layer, upon the liquid side, is movable, while the other is firmly attached to the layer of liquid which covers the surface of the capillary wall; further, that it behaves as if the difference in charge arises from the kations being in excess in the one layer and the anions in the other. An external E.M.F. therefore acts as it would upon ions, and causes a relative motion of the layers. The movable inner layer is displaced relatively to that upon the wall, and wanders, according to the sign of its charge, towards the positive or negative pole. In the stationary state the external electric force serves to overcome friction and to maintain the constant speed with which the volume of liquid transferred wanders to the one electrode.

The force of friction is proportional to the coefficient of viscosity of the liquid, to the surface causing friction, and to the velocity gradient. As coefficient of viscosity or internal friction, we may take that of the liquid η, since it is assumed that the double layer is entirely contained in the liquid. Let the surface be equal to unit surface. The mean velocity u corresponds to the length of the thread of liquid which exudes from the capillary in unit time, and of which the volume is v; hence we have

$$\pi r^2 u = v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This mean velocity holds in the whole interior of the tube. For at the surface where the electric force takes effect and overcomes the friction, that is, at the distance δ of the movable side of the double layer from the fixed

[1] Zeitschr. f. physik. Chemie, **79**, 385 (1912).
[2] See the older literature in *Wiedemann*, Elektrizität, I, 993 (1893).
[3] Pogg. Ann. **87**, 321 (1852); **99**, 177 (1856).
[4] Pogg. Ann. **113**, 513 (1861).
[5] Wied. Ann. **7**, 337 (1879); Gesamm. Abhandl. II, 855.
[6] Phil. Mag. (5), **25**, 52 (1888).
[7] Bull. Acad. Sciences d. Cracovie, 1903, p. 182. See particularly the comprehensive account by *Smoluchowski* in *Graetz*, "Handbuch der Elektrizität und des Magnetismus," Vol. II, p. 366 (1914).
[8] J. Chim. Phys. **2**, 601 (1904).

side thereof, the liquid already moves with velocity u, the remaining liquid in the tube is only dragged along with it. The gradient of velocity $\frac{du}{dz}$ (z = vertical distance to the wall) therefore lies entirely within the double layer. $\frac{du}{dz}$ can be put $= \frac{u}{\delta}$, for the movable side of the layer has velocity u, the fixed side zero, and δ is a small distance. The force of friction for the unit of surface is therefore when $u = \frac{v}{\pi r^2}$

$$\frac{\eta v}{\pi r^2 \delta}.$$

The electric force acting upon unit surface of the movable side of the double layer is equal to the charge e upon this unit of surface multiplied by the gradient of potential H produced by the external E.M.F. E. Hence

$$\mathrm{e} : \mathrm{H} = \frac{\eta v}{\pi r^2 \delta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we regard the double layer as a condenser of potential ζ in a medium of dielectric constant D, then according to a known law

$$\zeta = \frac{4\pi\delta \mathrm{e}}{\mathrm{D}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This, substituted in equation (2), gives for the liquid volume

$$v = \frac{r^2 \zeta \mathrm{HD}}{4\eta} = \frac{r^2 \zeta \mathrm{ED}}{4\eta l} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where l denotes the distance separating the external electrodes.[1]

If we have, instead of a single capillary, a bundle of section q or a diaphragm which can be regarded as such a bundle, then q is to be put in place of πr^2, and we get

$$v = \frac{q \zeta \mathrm{HD}}{4\pi\eta} = \frac{q \zeta \mathrm{ED}}{4\pi\eta l} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The amount of liquid transferred by electrosmosis is directly proportional to the cross-section of the tube, the difference of potential in the double layer, the external potential gradient, and the dielectric constant, and inversely proportional to the viscosity of the liquid.

Now $\mathrm{E} = iw$, where i is the current and w the resistance, and $w = \frac{l}{q\lambda}$, where l is the length of the capillary, q its cross-sectional area, and λ the specific conductivity of the liquid; hence

$$v = \frac{\zeta i \mathrm{D}}{4\pi\eta\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If the current is kept constant, the flow of liquid is independent of the length and area of the capillary.

If the liquid is not allowed to flow out, but instead to set up a hydrostatic pressure to balance the electric force, this pressure must be equal to that

[1] It is not, as we shall see later (p. 254), straightway correct and self-evident, that the distance between the layers should be equal to the quantity δ which determines the gradient of velocity, and so cancels out of the equation.

required to move the liquid in the opposite direction. If Poiseuille's law holds for the capillary or diaphragm, then we have

$$v = \frac{\pi P r^4}{8\eta l}$$

where P is the hydrostatic pressure. Hence in equilibrium, using equation (4),

$$P = \frac{2\zeta ED}{\pi r^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

With a given radius of tube and given properties of the walls, the height to which the liquid is raised is proportional to the applied E.M.F. ; when the radius varies the height of rise is inversely proportional to the square of the radius.

The experiments given in Table 78 from Quincke [1] and Tereschin [2] show how far these laws hold. They were performed with an arrangement like that of Fig. 43, except that the diaphragm consisted of a single glass capillary. The movements of the liquid, in part very small, were observed against a fine scale by means of a microscope with micrometer eyepiece, at room temperature.

If equation (7) holds, ζ, the potential of the glass against the liquid (distilled water), should be constant. In calculating ζ we must note that everything must be expressed in absolute measure. One absolute electrostatic unit of potential (the use of which was implied in arriving at equation (2)) is equal to 300 volts ; hence E in volts must be divided by 300, and the resulting value of ζ multiplied by 300 to bring it to volts. In other words, the value of ζ deduced from (7), putting E in in volts, must be multiplied by $(300)^2$ to bring it to volts.

TABLE 78

Dependence of Electrosmotic Flow upon Radius of Capillaries and External E.M.F.

r (cm).	Δh (cm.) [3].	ϕ.	E (volts).	ζ (volts).	Observer.
0·0449	0·0125	5° 26′	76	0·054	Quincke
0·0449	0·0245	5° 26′	152	0·053	,,
0·0188	0·0880	9° 7′	154	0·055	,,
0·0944	0·0104	2° 39′	148	0·050	,,
0·0369	1·9	2° 56′	5,120	0·041	Tereschin
0·0369	3·1	2° 56′	7,220	0·048	,,
0·0369	3·8	2° 56′	8,860	0·048	,,
0·0369	4·3	2° 56′	10,200	0·046	,,
0·0369	4·8	2° 56′	11,500	0·046	,,

In the case of diaphragms it is always necessary to test whether they obey Poiseuille's law. This holds to a large extent for plates of clay ;

[1] *loc. cit.* p. 241.

[2] Wied. Ann. **32**, 333 (1887).

[3] The height of rise of the liquid in the measuring capillary is equal to the measured displacement Δh times the sine of the angle φ at which the tube is inclined to the horizontal. Only those experiments of *Quincke* and of *Tereschin* are comparable among themselves, which were carried out with one and the same diaphragm capillary.

hence it is natural that the experiments of Wiedemann, according to Helmholtz, fulfilled theoretical expectation.

We will now take the case of *kataphoresis, the transport of suspended particles by the electric current.*

In order to ascertain the velocity of the particles, consider a small cylinder fixed in a capillary of larger radius than the cylinder. The liquid therefore streams through an annular canal past the cylinder. Its velocity is, if we combine (4) with (1), and regard the annular canal as a system of tubes,

$$u = \frac{\zeta \mathrm{HD}}{4\pi\eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

independently of the section. This is natural when we recollect that the movable layer carried along by the external E.M.F. carries with it the whole interior liquid. A lower limit for the validity of the formula is reached when the breadth of the tube is no longer large compared with the distance between the two sides of the double layer.

If the small solid cylinder is movable, it must move, according to the law of action and reaction, with the same velocity $u = \frac{\zeta \mathrm{HD}}{4\pi\eta}$ in the opposite sense. In this argument no assumptions are made as to size and shape of the body, hence the velocity must be independent of these. This is evident when we consider that the quantities which determine the velocity in the stationary state, viscosity coefficient, velocity gradient, double layer, external potential gradient, are independent of the size and shape of the body, and that eddies and the like do not occur.

The kataphoretic migration velocity can be measured with moderate accuracy macroscopically, by placing the emulsions, suspensions, or colloidal solutions, the particles of which wander kataphoretically, in a U-tube, as Burton [1] did (Fig. 44). By first introducing some pure solvent, and then the liquid to be investigated, we can arrange by cautiously opening the tap that the electrodes E and E′ dip into the pure solvent, and a clearly visible boundary between the two liquids is formed. The boundary which moves away from the electrode becomes still sharper after applying the current, as will be explained later (cf. p. 396). The distance traversed by the boundaries in a given time is determined against a scale. Too long times must not be taken, otherwise the influence of impurities formed by electrolysis makes itself felt. Coehn's [2] kataphoresis tube (Fig. 45) is very much to be recommended.

More exact is the microscopic method as developed by Ellis [3] and Powis,[4] and particularly the ultra-microscopic arrangement of Svedberg and Andersson.[5] Ellis and Powis followed with a microscope the motion of a single suspended particle, a drop of oil, which was between the slide and the cover-glass. Svedberg and Andersson worked out two different methods. In the first case, in order to avoid the disturbances due to electrolysis, which are the greater the longer the current is passed, they only allowed

[1] Phil. Mag. (6), **11,** 440 (1906).

[2] Zeitschr. f. Elektrochemie, **15,** 653 (1909). Concerning an altered form of this device, in which by reversing the current electrolyte which may have been decomposed is restored to its original condition, see *Steigmann,* Kolloidzeitschr. **27,** 37 (1920).

[3] Zeitschr. f. physik. Chemie, **78,** 321 (1912).

[4] *Ibid.* **89,** 91 (1915).

[5] Kolloidzeitschr. **24,** 156 (1919).

short impulses of current to act upon the particles, and photographed their path, using an ultra-microscope with paraboloid condenser (see p. 389). The disturbances due to electrolysis can be still more effectively avoided by using alternating current. The colloid particles thus respond to small E.M.F.'s, and so instantaneously that in the alternating field their diffraction images under the ultra-microscope are drawn out into lines of light. This was first observed by Cotton and Mouton [1]; they found that even at 1280 periods per second the particles followed the current changes perfectly. From the length of the lines of light and the periodicity Svedberg and Andersson deduced the velocity of the particles.

In all these microscopic methods, in which a comparatively thin layer of liquid in a cell is observed, the following circumstance must be taken into

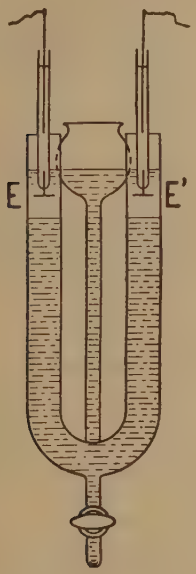


Fig. 44.

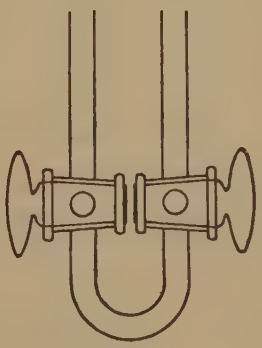


Fig. 45.

account. Under the influence of the current electrosmosis takes place along the walls of the cell, and the particles are carried along by the moving liquid. The observed velocity u' of the particles is by no means the true one, u, determined solely by kataphoresis, but the sum of the latter and the true (not mean) velocity U of the liquid; hence

$$u' = u + U \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Only in very broad troughs, at least 2 mm. wide, can the velocity of the liquid in the middle of the chamber be neglected, and the velocity of the particles there observed be taken as the true one. With thin chambers, such as are used for ultra-microscopic measurements (Svedberg and Andersson used such 50–70μ thick), this influence must certainly be taken into account.

v. Smoluchowski [2] has developed a theory of the phenomenon. From the general formula for the velocity of a liquid under the influence of electros-

[1] Compt. rend. **138**, 1504 (1904).
[2] *Graetz*, "Handbuch d. Elektrizität u. d. Magnetismus," II, 2, p. 382 (1914).

mosis we get for U the following dependence upon the distance x from the walls of the cell, which are parallel to the direction of motion, and at right-angles to that of observation:

$$U = U_0\left[1 - 6\left\{\frac{x}{d} - \left(\frac{x}{d}\right)^2\right\}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Here U_0 is the velocity directly at the cell wall, d the thickness of the chamber.

If we observe the apparent velocities u'_a and u'_b of the particles at the distances a and b, U_a and U_b may be calculated from equation (10) as functions of U_0. We have, therefore, two equations with two unknowns, u and U_0, from which the true velocities of the particles and of the liquid at the cell wall can be calculated. It is not good to measure one velocity immediately against the upper cell-wall, since there a correction for the influence of the wall must be taken into account; this may be avoided by measuring at different distances from the wall, for example, at $\frac{1}{2}$ and $\frac{1}{6}$ of the thickness of the liquid layer. We then get

$$u = \frac{3}{4}u'_{\frac{1}{6}} + \frac{1}{4}u'_{\frac{1}{2}}$$

or we measure u' at the bottom, where $U = 0$ and hence $u = u'$.

If u' is expressed as a function of x, the formula gives a parabola. Svedberg and Andersson were able to confirm Smoluchowski's theory satisfactorily. It appeared from their results that the alternating-current method gives more exact results than the method of short direct-current impulses.

The microscopic measurements of Ellis and Powis also give the kataphoretic velocity of the particles as well as the electrosmotic velocity of the liquid.

In the following, the results of kataphoretic experiments upon particles of colloidal solutions will be unhesitatingly employed as examples, since they show no difference as compared with the kataphoretic movement of coarser particles.

Of the reverse phenomena, *stream-potentials, currents due to falling particles*, etc., the first-named has been particularly investigated. If a liquid is forced through a capillary by the excess of pressure P, then electrodes arranged at either end of the capillary exhibit a potential difference E against each other. According to Helmholtz, the following relation holds for E:

$$E = \frac{P\zeta D}{4\pi\eta\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

(The letters have the same significance as before.)

Stream-potentials are particularly suited for determining the influence of the nature and concentration of dissolved substances. The capillaries can be easily changed and cleaned, and fewer disturbances by electrolytically produced subtances are to be feared. The method of measurement used by Kruyt [1] was modified by Freundlich and Rona [2] so as to allow the influence of various substances upon an electrokinetic phenomenon to be followed very conveniently. The capillary K (Fig. 46) can be easily removed and changed by means of ground joints; the liquid is driven in a strong current

[1] Kolloidzeitschr. **22**, 81 (1918).
[2] Sitzungsber. Preuss. Akad. Wiss. **20**, 397 (1920).

by the pressure from a gas cylinder out of the spherical containers B and B′ through K. The use of reversible calomel electrodes E and E′ is important; these were connected with the stream space by means of tubes containing KCl-agar jelly. As electrometer a quadrant or binant instrument is to be recommended.

We must regard as similar to stream currents those currents which arise when we allow a liquid to stream over an electrode, while the other one, symmetrically disposed, is at rest in the same liquid. Helmholtz [1] made experiments of this kind with platinum in sulphuric acid, Billiter [2] with mercury electrodes in various aqueous solutions. Quantitative measurements were not carried out. The older experiments of Dorn,[3] Billiter,[4] Mäkelt [5] on currents from falling particles were merely qualitative; quantitative ones are due to J. Stock,[6] who was able to confirm the formula

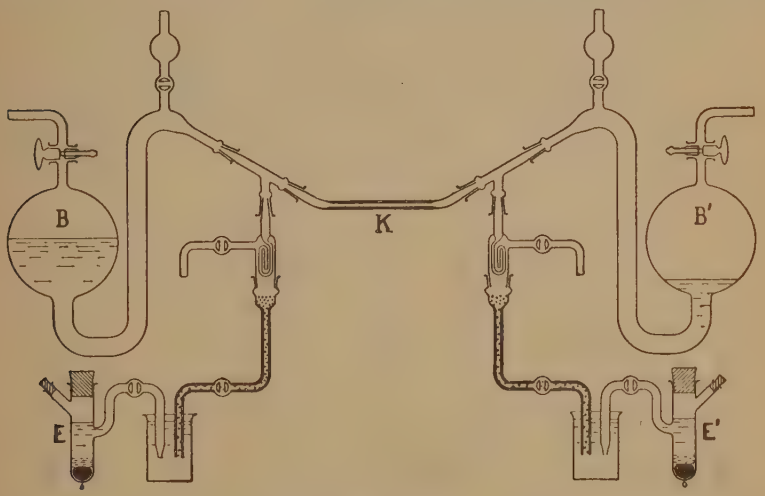


Fig. 46.

developed by v. Smoluchowski. He allowed fine quartz powder to fall down in nitrobenzene, ether, and toluene, without touching the electrodes, which were arranged laterally. The experiments on currents with moving electrodes can only be employed with caution, since in all cases in which the electrodes themselves are concerned any asymmetry can produce a current.

Since in the following pages repeated use will be made of the fact that electrosmosis, kataphoresis, stream-potentials, and so forth, are very closely linked together in the manner just set forth according to Helmholtz' theory, a numerical proof of the justification of this view may not be out of place. Saxén [7] determined with one and the same apparatus the electrosmotically transferred volume v and also the potential E of the stream current. He

[1] *loc. cit.* p. 241.
[2] Zeitschr. f. physik. Chemie, **48**, 542 (1904).
[3] Wied. Ann. **10**, 70 (1880).
[4] Ann. d. Physik (4), **11**, 937 (1903).
[5] *Freundlich* and *Mäkelt*, Zeitschr. f. Elektrochemie, **15**, 161 (1909).
[6] Anzeiger d. Akad. d. Wiss. Krakau A. **1913**, 131; **1914**, 95.
[7] Wied. Ann. **47**, 46 (1892).

used as diaphragm a clay plate, as liquids solutions of zinc, cadmium, and copper sulphates with electrodes of the corresponding metal, so that no disturbances due to polarization were to be feared.

From equation (6), p. 242, for electrosmosis, and equation (11), p. 246, for the stream-potential, it follows that

$$\frac{v}{i} = \frac{E}{P}$$

if wall and solution are the same in both cases.

The following table shows how far this is the case.

As regards the dependence of electrosmosis upon temperature, Cruse [1] has made experiments with distilled water and clay diaphragms and found that a maximum of liquid transferred occurs at about 40°; v. Smoluchowski [2] points out that in formula (6), p. 242, ζ, η, and λ all depend upon temperature.

TABLE 79

Comparison of Electrosmosis and Stream-potential

Solution.	$\frac{v}{i}$	$\frac{E}{P}$
0·0174 mol. $ZnSO_4$	0·360	0·352
0·0261 „ $ZnSO_4$	0·382	0·379
0·0348 „ $ZnSO_4$	0·346	0·344
0·0195 „ $CdSO_4$	0·582	0·588
0·0390 „ $CdSO_4$	0·116	0·115
0·0400 „ $CuSO_4$	0·385	0·385
0·0800 „ $CuSO_4$	0·233	0·237

If we assume ζ to be constant, then the expression $\frac{1}{\lambda\eta}$ exhibits a temperature relation which is quite similar to that of the liquid transferred.

In the case of kataphoresis, where the conductivity does not enter directly into the equation (see equation (8), p. 244), it is chiefly the viscosity which changes with temperature. If ζ and D are assumed to be fairly independent of the temperature, ηu should according to the above equation be constant at different temperatures. According to some experiments by Burton [3] on the kataphoresis of colloidal aqueous silver solutions, this is the case, as the following table shows.

TABLE 80

Influence of Temperature on Kataphoresis

t.	η.	u in cm./sec. for 1 volt/cm.	$\eta \cdot u$.
11°	0·01282	$1{\cdot}96 \cdot 10^{-4}$	$2{\cdot}51 \cdot 10^{-6}$
21°	0·00992	$2{\cdot}52 \cdot 10^{-4}$	$2{\cdot}52 \cdot 10^{-6}$

[1] Physik. Zeitschr. **6**, 201 (1905).
[2] Physik. Zeitschr. **6**, 529 (1905).
[3] Phil. Mag. (6) **11**, 440 (1906).

Influence of Electrokinetic Phenomena on Conductivity

v. Smoluchowski[1] has pointed out that electrosmosis and kataphoresis must necessarily change the conductivity. In the case of electrosmosis, the electrically charged layer lying against the wall of the capillaries is moved by the current. We have there a surface conduction, which is added to the galvanic conduction in the interior of the liquid. If the galvanic conductivity is great, as in somewhat concentrated aqueous solution, this electrosmotic surface conduction may be neglected in comparison, but it may become comparable to it in the case of weakly conducting liquids, such as nitrobenzene and aniline.

J. Stock[2] observed this phenomenon in comparing the conductivity of nitrobenzene, aniline, and other such substances, as usually measured, with that found when the space between the electrodes was filled with fine quartz powder soaked in the liquid. The powder was purified and dried as carefully as possible. In its presence the current was considerably greater, up to about twenty times greater with the finest powder, the particles of which had a radius of about 1μ.

The formula derived by v. Smoluchowski for the case of a capillary traversed by a current is

$$\frac{i_w}{i_q} = \frac{\omega}{q\eta\delta\lambda}\left(\frac{D\zeta^2}{4\pi}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

i_w is the strength of the surface conduction current, i_q that of the ordinary galvanic current, ω is the circumference, q the sectional area of the tube, λ the specific conductivity, η the viscosity, δ the thickness of the double layer, ζ the potential of the double layer, D the dielectric constant. With suitable transformation the equation may be applied to the experiments of J. Stock. It is notable that both the thickness δ of the double layer and the potential ζ occur in this expression. If ζ is known from other electrosmotic measurements, δ may be calculated. In the most trustworthy measurements with a quartz powder of $6{\cdot}5\mu$ radius, a thickness of the double layer $\delta = 4{\cdot}5\mu\mu$ was obtained, ζ being about 0·050 volt.

The conductivity of a suspension must also be greater on account of the kataphoresis of the suspended particles. For although each particle is enveloped in a double layer, the current always produces a displacement of the double layer; the charges move towards the two poles, and part of the current must be carried by them. For the specific conductivity (in reciprocal ohms) of a suspension, the particles of which had a radius r, the following formula was obtained:

$$\lambda = \frac{4\pi\nu\eta r(r+\delta)u^2}{N\delta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here ν is the number of particles per c.c., u their kataphoretic velocity with a gradient of 1 volt per centimetre, N Avogadro's number, η and δ have the usual signification.

How far this equation must be taken into account in the conductivity of sols is discussed on p. 395.

[1] Anzeiger. d. Akad. d. Wiss. Krakau, **1903,** p. 185; Physik. Zeitschr. **6,** 529 (1905).

[2] Anzeiger d. Akad. d. Wiss. Krakau A. **1912,** p. 635.

The Properties of the Electrical Double Layer acting in Electrokinetic Phenomena

The electrokinetic phenomena in aqueous solution are extraordinarily strongly affected by small concentrations of dissolved substances.. If the boundary surface is sufficiently small, say with a single capillary, millionths of a mol (micromol) of many electrolytes produce sensible effects. Since, under these conditions, the dielectric constant [1] and the viscosity are scarcely different from those of pure water, the potential difference ζ is the sole quantity occurring in the equations in the previous section, which can be so greatly altered. We will, therefore, first discuss what the nature of this potential difference is, and how it is connected with the potential difference ε, which Nernst's theory assumes to exist at the interface metal —solution.

That in electrokinetic phenomena we are usually dealing with a potential difference at the surface of a non-metal and in the case of Nernst's potential difference at that of a metal, must not be regarded as an essential variation. In the first place, exactly the same regularities have been found in the kataphoresis of metallic particles and in currents due to falling metallic particles, as in the case of the electrokinetic phenomena of non-metallic particles, and this is, moreover, very decidedly the case as regards the influence upon ζ of dissolved substances. Then the view that we may regard non-metallic oxide or carbon electrodes as oxygen-hydrogen electrodes, in the Nernst sense, has proved entirely satisfactory. Haber and Klemensiewicz [2] were able to regard even glass itself as such an electrode and to measure its potential against aqueous solutions in the manner used for measuring potential differences in galvanic cells. Their experimental arrangement is shown in Fig. 47; the thin-walled glass bulb A (thickness, 0·06 to 0·1 mm.) dips into a solution of an electrolyte in the beaker B, the $H^{\cdot}$ and OH'-ion content of which could be varied. The bulb contains any electrolyte (acid or KCl solution) in which an electrode connected with an electrometer is placed. Into the beaker B dips a normal electrode E, usually earthed. The potential of the glass altered in a perfectly regular fashion with the $H^{\cdot}$ and OH'-ion content of the solution and could to a great extent be interpreted by assuming upon the surface of the glass an imbibition layer which behaved like a hydrogen or OH' electrode of constant concentration.

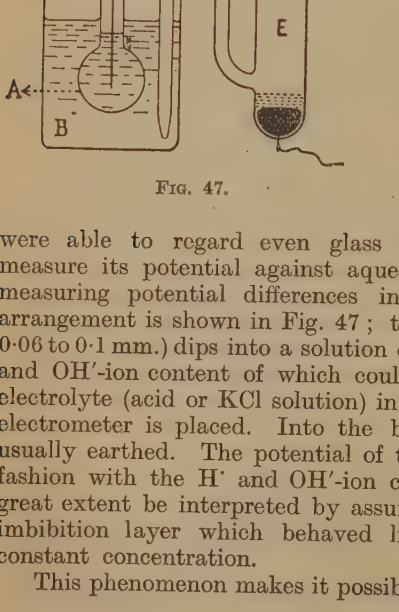


Fig. 47.

This phenomenon makes it possible to measure the potential differences

[1] See *Smale*, Wied. Ann. **60**, 625 (1897).

[2] Zeitschr. f. physik. Chemie, **67**, 385 (1909). *Cremer* [Zeitschr. f. Biolog. **47**, 562 (1906)] was the first to investigate such cells, after *Helmholtz* [J. Chem. Soc. **39**, 292 (1881)] had shown the applicability of glass as an electrolytically conducting intermediate layer.

ε and ζ on one and the same material, to determine their dependence upon the nature of the substances in solution, and to investigate the relation in which they stand to one another. For this purpose Freundlich and Rona [1] determined on the one hand ε with glass bulbs by Haber and Klemensiewicz' method, and at the same time ζ by the help of stream-potentials in glass capillaries—in part of the same glass as that of which the bulbs were made—using the arrangement described on p. 247. The result was that ζ was found, in accordance with earlier experiments, to be extremely sensitive to small concentrations of foreign substances; $H^{\cdot}$-ions, in a concentration measured in micromols, produce a 50 per cent. depression of the negative charge of the capillary wall against pure water, without however reversing the sign of the charge in higher concentrations; this occurred with aluminium chloride in concentrations of 1 to 2 micromols, and with crystal violet at 50 micromols. In the measurement of ε nothing could be seen of these influences. In agreement with Haber and Klemensiewicz it depended entirely upon the $H^{\cdot}$-ion concentration. If aluminium chloride or crystal violet were added to pure water, ε changed only in so far as the $H^{\cdot}$-ion concentration changed, hence considerably less than if the $H^{\cdot}$-ion was added in the same molar concentration. If the $H^{\cdot}$-ion concentration was kept constant with help of a buffer-mixture (sodium acetate + acetic acid) substances such as aluminium chloride and crystal violet produced no change even in concentrations of some hundreds of micromols.

It follows from these experiments that ζ and ε are certainly not identical. Hence the conclusions of Billiter,[2] which depended upon the identity of the two quantities, are undoubtedly incorrect. He hoped to be able to determine the absolute zero of electric potential by bringing the ζ of metallic particles to zero by changing the metal-ion concentration, in kataphoretic experiments and experiments with falling particles. In this way he believed he could measure single potential differences. His zero-point differed, however, by more than half a volt from that of Helmholtz, which, as is well known, is deduced (cf. p. 297) from the electrocapillary curve of mercury against aqueous solutions, and depends essentially upon the difference of potential ε. This absence of agreement is by itself a proof that ε and ζ are not identical. A comparison of the experiments of Haber and Klemensiewicz with those of Cameron and Oettinger [3] is likewise in favour of this view. Haber and Klemensiewicz found, in measuring the potential of glass against solutions (therefore the potential difference ε), that it becomes less by 0·43 volt when we pass from a $_{20}^{1}{}_{0}$ normal alkali solution to a $_{20}^{1}{}_{0}$ normal acid solution; measurements by Cameron and Oettinger of stream-potentials in glass capillaries gave under similar experimental conditions and with the same solutions a decrease of only 0·015 volt.

But it is entirely comprehensible that the electrokinetic difference of potential ζ and the difference of potential ε, which may be designated phase-boundary force (Phasengrenzkraft), are not identical. The forces which are exerted in the electrokinetic experiments, in order to move the two sides of the layer relatively to one another, are by no means great enough for the liquid to be torn off the surface of the solid. For this reason, indeed, it was assumed at the outset (cf. p. 241) that the mobile layer of liquid towards

[1] *loc. cit.* p. 246.

[2] Zeitschr f. Elektrochemie, **8**, 638 (1902); **15**, 439 (1909); Zeitschr. f. physik. Chemie, **45**, 307 (1903); **48**, 513 (1904); **49**, 709 (1904); **51**, 167 (1905); Ann. d. Physik (4), **11**, 913 (1903).

[3] Phil. Mag. (6), **18**, 586 (1909).

the interior moves against the layer of liquid adhering to the solid surface, and not against that surface itself. But since one side of the Nernst double layer is situated in the solid surface, and not in the liquid layer adhering to it, the two sides of this double layer are certainly not moved relatively to one another. On the contrary, we must rather picture the state of affairs as follows. The two layers of the double layer do not always lie, as has been generally assumed, at a distance equal to the diameter of a molecule from one another; the double layer frequently stretches much further out from the solid surface into the liquid. A double layer of this kind may be described, following Gouy,[1] as *diffuse*. A part lies, therefore, in the liquid firmly adhering to the solid surface, another part in the movable liquid. ε is the difference of potential between the solid and the movable liquid, ζ that between the liquid adhering to the wall and the movable liquid. From Fig. 48, after v. Smoluchowski,[2] who also reached this view, the relationships are easily seen. In it we must imagine to the left of A the solid wall, to the right of B the movable liquid, between A and B the film of liquid adhering firmly to the wall; the abscissæ are the distances from a point in the solid wall, the ordinates potentials. When we measure potentials of galvanic cells, by an experimental arrangement which may be called transverse, since we measure, as it were, at right-angles to the double layer, we find the total fall of potential between the solution and the solid phase, say glass, $\varepsilon = \varepsilon_s - \varepsilon_f$. In electrokinetic experiments, in which we measure, figuratively speaking, tangentially (that is, with help of a current in a tangential direction), the result depends only upon the fall of potential between the movable liquid and the firmly adhering film of liquid $\zeta = \varepsilon_h - \varepsilon_f$.

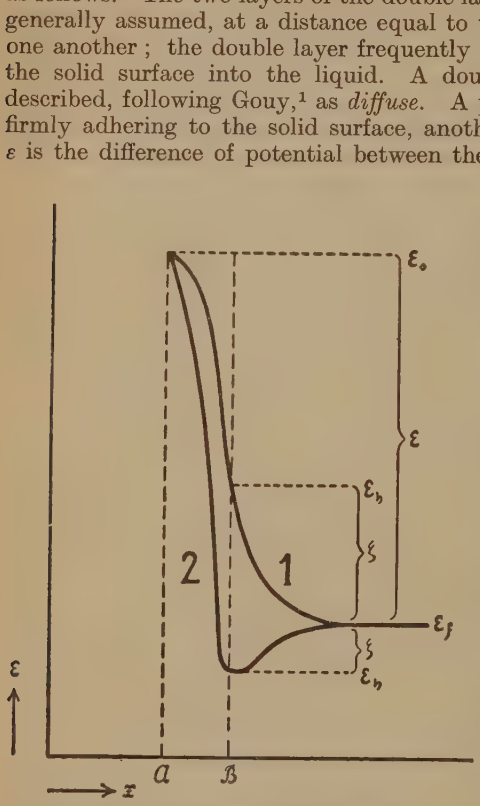


FIG. 48.—Fall of Potential at the Surface of a Solid Wall against a Liquid.

A further consequence of these experiments is that the dielectric constant must be introduced into the theory of electrokinetic phenomena, as has been done above; for ζ is to fall entirely within the liquid, and the distance between the layers is to be greater than the diameter of one molecule. Helmholtz did not take the dielectric constant into account in his theory, probably because he assumed too small a distance between the layers. Taking the dielectric constant into account we reach values of ζ of $\frac{1}{100}$

[1] J. d. Phys. (4), **9**, 457 (1910). The idea of introducing a double layer of greater thickness is due to *Billiter* [Zeitschr. f. physik. Chemie, **45**, 307 (1903)]; he spoke of a dissociation of the double layer.

[2] See *Graetz*, "Handbuch d. Elektrizität u. d. Magnetismus," II, p. 393 (1914).

to $\frac{1}{10}$ volt (cf. Table 81), so that the conception of ζ as a part of ε appears quite comprehensible; according to Helmholtz we get ζ values 80 times larger, of 5 to 10 volts, which cannot be reconciled with the ordinary values of ε. Pellat[1] was the first to demand the introduction of the dielectric constant.

Before Freundlich and Rona, Borelius[2] had compared transversely measured potentials with tangentially measured ones, using as his transverse measurements determinations of the phase-boundary force between paraffin and aqueous salt solutions, which he had carried out by an electrostatic method[3]; for comparison he took the kataphoretic measurements of Powis on drops of paraffin oil. The experiments do not permit of such definite conclusions as those on glass electrodes, since the phase-boundary force on paraffin has not the character of a Nernst potential difference for a metal, but is rather to be regarded as a potential difference arising from the distribution of ions at a boundary surface (cf. p. 255). As will be discussed later (cf. p. 273) a curve for the potential at the boundary similar to curve 1 in Fig. 48 is to be expected, that is, a considerable symbasis between ε and ζ. This is also found in the experiments of Borelius. The only difference is that at high concentrations ζ becomes small or zero, ε does not. Borelius correctly explains this as arising from the thickness of the diffuse double layer becoming small at high concentrations.

While, as we have said, in the case of phase-boundary forces which depend upon a distribution of the ions, a parallelism between ε and ζ seems frequently to hold, unpublished researches by Gyemant seem to indicate that this is not the case for oxidation-reduction potentials, and that in their case the course of the potential is rather according to curve 2 in Fig. 48. Substances such as Br_2, H_2O_2, and others, which are able to charge up a carbon electrode strongly, appear to be inactive in kataphoretic experiments in which carbon surfaces are used.

Gouy[4] has advanced some considerations concerning the diffuse double layer, which already give us important information concerning its properties. In the Helmholtz double layer the one side is situated in the solid wall, the other is in a very thin surface, which is opposite the former, inside the liquid, at a distance of one molecular diameter; in this thin layer the concentration of the one kind of ion, say the kations, is zero, if the negative layer lies in the liquid. In the diffuse double layer, on the other hand, the layer in the liquid is distributed therein as a space charge over a thicker boundary layer opposite the layer of opposite sign; in it there is (if it be a negative layer) only an enrichment in respect of anions, and a depletion in respect of kations. The enrichment and depletion decrease asymptotically as we move towards the interior of the solution. Gouy calculates the equilibrium which is set up when one kind of ion is moved by electric forces towards or away from the boundary surface, while, on the other hand, the osmotic forces strive to bring about equality of concentration in all parts. The influence of adsorption, which independently of electrical influences must cause a displacement of ionic concentration, is recognized

[1] In *Perrin's* paper, *loc. cit.* p. 241.

[2] Ann. d. Physik (4), 50, 447 (1916).

[3] Ann. d. Physik (4), **42**, 1129 (1913); **45**, 929 (1914); **53**, 239 (1917); Lunds Universitets Årsskrift, N.F., Afd. 2, **11**, No. 5 (1915).

[4] *loc. cit.* p. 252; see also Compt. rend. **149**, 654 (1909); Ann. d. Physik (9), **7**, 129 (1917).

by Gouy as important, but neglected for the present. Let N_K and N_A be the number of anions and kations in unit volume in the interior of the solution, assuming only these two ions to be present; let α_K and α_A be the coefficients with which N_K and N_A must be multiplied in order to calculate the number of ions in unit volume in the neighbourhood of the surface. α_K and α_A alter with the distance z from the surface—the one coefficient is greater, the other less than unity. Let $\mathbf{e}$ be the charge per unit of surface at a distance z, to which α_K and α_A correspond. D is the dielectric constant. We then get

$$N_K(\alpha_K - 1) + N_A(\alpha_A - 1) = \frac{2\pi \mathbf{e}^2}{DRT} \cdot \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It results from this equation that we may obtain the same effect by imagining the charge in the electrolyte to be concentrated in a centre of gravity (as it were), that is, in an extremely thin surface, which is to be regarded as the second layer. The diffuse double layer may thus be replaced by a Helmholtz one, which must then have a thickness δ ascribed to it, which varies within wide limits, since the distance of the centre of gravity of the layer from the boundary surface is very variable. We get, as is easily seen, the result that δ is smaller, the greater the charge and the greater the ionic concentration; we then soon arrive at values as small as those given by the Helmholtz double layer. For small charges and small ionic concentrations δ acquires considerable values. Thus Gouy calculates for an interfacial charge of $\mathbf{e}_0 = 10$ electrostatic units the following values of δ:

Solution $\frac{1}{10}$ normal in ions $0{\cdot}96\mu\mu$.
Solution $\frac{1}{1000}$ normal in ions $9{\cdot}6\mu\mu$.
Pure water (Kohlrausch) $1010\mu\mu$.

With small charges we must reckon with considerable values of δ for solutions with a concentration below 1 millimol per litre.

The theory of the diffuse double layer has not yet been worked out for strongly adsorbable ions. Since the attraction by the boundary surface due to adsorption acts in the same direction as the electric attraction, the result will be similar to that brought about by a higher charge; that is, also for small concentrations the thickness δ will be smaller than it would be for capillary inactive electrolyte solutions of the same concentration.

Regarding the dependence of the electrokinetic phenomena upon the concentration and nature of the electrolyte present in the solution, the following may be surmised on the basis of this view of the diffuse double layer. At high concentrations of electrolyte the electrokinetic phenomena will become insignificant and will disappear for the simple reason that the double layer will no longer reach far enough into the liquid; at the point where the layer of liquid adhering to the wall passes over into the movable liquid, appreciable differences of potential will no longer exist. Besides this influence, the increase in conductivity causes a diminution in electrokinetic action. For the phase-boundary force ε, only those ions will play a part which can also pass over into the solid wall; that is, metallic ions of the same metal in the case of a metallic wall, $H^{\cdot}$ and OH'-ions in the case of glass, and so forth; and it will be largely independent of foreign ions, particularly those of the same sign. Such foreign ions will only exert an influence when they change the metal-ion concentration in the solution, by forming, for instance, a difficultly soluble salt or a complex ion. This is

well known for the potential of a metal in a solution of its own ions, and was also found for glass electrodes in the above-mentioned experiment of Freundlich and Rona. ζ, on the other hand, will be determined by all ions which are present in the boundary layer, no preference being accorded to the ions determining ε; rather their charge and adsorbability will be of importance.

As has been pointed out, the course of the potential curve need not be as simple as curve 1, Fig. 48; it might very well correspond to curve 2. If on changing the concentration of the ions in the solution the potential curve passes from 1 into 2, then ζ passes through the value zero; we have Billiter's zero of potential, which is entirely different from that of Helmholtz, since ε need not become zero under the same conditions. It is not even necessary that the potential metal-metallic ion should change much. Thus, Mäkelt[1] found for currents caused by falling silver particles that the charge of the firmly adhering layer on the wall in a weakly acid $AgNO_3$ solution was positive; it was negative, on the other hand, when the solution was made weakly alkaline with NH_3, while the potential Ag-Ag$^{\cdot}$-ion remained practically unaltered at 0·4 volt.

Dependence of the Electrokinetic Processes in Aqueous Solution upon the Nature of the Solid Phase

In accordance with the discussion in the last section we shall in future always distinguish between:

1. The wall-charge, or charge of the solid body itself.
2. The wall-layer charge, that is, the charge of the film of liquid adhering to the wall, which forms the external coating for the double layer ζ.
3. The charge of the moving liquid, which forms the inner coating of this double layer.

In pure water the wall-layer for the great majority of solids and non-miscible liquids is charged *negatively* with respect to the movable liquid. Water therefore moves by electrosmosis towards the negative pole[2] in capillaries of glass, quartz, and shellac, and through diaphragms of clay, carborundum, asbestos, wool,[3] silk,[3] cotton,[3] arsenic trisulphide, etc. In kataphoresis, particles of clay, quartz, shellac, starch, lycopodium, graphite, etc., are driven towards the positive pole, likewise the particles in colloidal solutions of silver, gold, platinum, selenium, sulphides such as As_2S_3, Sb_2S_3, and many others; and in the case of stream-potentials positive electricity moves with the water in capillaries of glass, silver, and platinum.

The wall-layer is charged positively only with comparatively few oxides or hydroxides, halides, carbonates, and others; for example, ZnO, CoO, $CrCl_3$, $BaSO_4$, $BaCO_3$, etc. Approximately the rule applies that the wall-layer is negatively charged in the case of weakly acid substances, and positively in the case of weakly basic ones.

How this comes about is perhaps most easily seen from the behaviour of a substance such as glass. Glass, according to the consideration on p. 207, is an amorphous solid electrolyte with a sluggish anion and easily mobile

[1] *loc. cit.* p. 247.
[2] Concerning the following data, see *Quincke, loc. cit.* p. 241; *Perrin, loc. cit.* p. 241.
[3] *Larguier des Bancels,* Compt. rend. **149,** 316 (1909).

kation (a metallic ion, probably of an alkali metal). Nernst,[1] Haber,[2] and particularly L. Michaelis,[3] have worked out how the solution tensions of kation and anion Π_K and Π_A may be distinguished in the case of such a binary substance, and that at the surface a phase-boundary force ε will be set up :

$$\varepsilon = RT \log \frac{\Pi_K}{P_K} = - RT \log \frac{\Pi_A}{P_A} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where P_K and P_A are the osmotic pressures of the two ions in the solution. The mobile kation has a greater solution tension, compared with the sluggish anion. *The solid glass will therefore be charged negatively to the solution* ; in the latter, as a result of the diffuse double layer, a gradient of kations will be present. Now we may perhaps assume that the gradient of potential has a simple regular course such as that represented by curve 1, Fig. 48 ; the firmly adherent layer will doubtless consist of glass which has imbibed water, and will therefore, apart from its larger water content, scarcely differ in its properties from the main bulk of the glass. ζ will therefore, as curve 1 in Fig. 48 shows, correspond in sign to ε, only being somewhat smaller (Haber and Klemensiewicz, Cameron and Oettinger, *loc. cit.* p. 251).

Many difficultly soluble weakly acid substances will behave similarly to glass. They become negatively charged, since the solution tension of the H'-ion is greater than that of the sluggish anion. Conversely, for difficultly soluble basic substances the OH'-ions will have the greater solution tension, and the particles will remain positively charged. For many substances, such as the hydroxides of Al, Fe, Th, it is also very probable that the wall-layer as imbibition layer is entirely like the solid substance and the potential curve has a simple course ; that is to say, the wall-layer has the same (positive) charge against the mobile liquid as the solid body.

In other cases, such as sulphides and the like, one is more inclined to believe that some kind of complex ion (polysulphide ion or also an anion containing oxygen) behaves as sluggish ion at the boundary surface.

It is still for the present difficult to understand that the particles of the noble metals, copper, silver, gold, and so on, have invariably a negative charge in pure water. One might have expected that the low solution tension of these metals would bring about a positive charge upon the solid wall of the particle. If we had a simple course of potential, like curve 1, Fig. 48, the adherent wall-layer would also be positive toward the moving liquid. Since this is not the case, we may draw the conclusion that the potential curve takes a less simple course, and corresponds say to curve 2 of Fig. 48. It is, however, perhaps still a doubtful question whether the surface of these particles is really metallic (p. 375).

We are, it may be remarked, still without a systematic investigation of the electrokinetic charge of the various solids, and the causes which condition it.

As regards the numerical value of the P.D. ζ in pure water, Table 78 gives a value of about $-0{\cdot}050$ volt for glass. The following table, which gives values for various substances deducible from kataphoretic experiments, shows that these also lie mostly between 30 and 100 millivolts.

[1] Zeitschr. f. physik. Chemie, **9**, 137 (1892).
[2] Ann. d. Physik (4), **26**, 927 (1908).
[3] "Dynamik der Oberflächen," Dresden, 1909, p. 49 *et seq.*

TABLE 81

ζ-Values for Various Substances in Pure Water

Suspended Body.	Diameter of Particles.	u in cm./sec. for Gradient 1 volt/cm.	ζ (in volts).	Observer.
Lycopodium	35μ	$2{\cdot}5 \cdot 10^{-4}$	− 0·037	Quincke [1]
Arsenic trisulphide (colloidal sol)	below $50\mu\mu$	$2{\cdot}2 \cdot 10^{-4}$	− 0·032	Linder & Picton [2]
Quartz.	1μ	$3{\cdot}0 \cdot 10^{-4}$	− 0·044	Whitney & Blake [3]
Prussian blue (colloidal sol).	below $100\mu\mu$	$4{\cdot}0 \cdot 10^{-4}$	− 0·058	,,
Gold ,, .	,,	$4{\cdot}0 \cdot 10^{-4}$	− 0·058	,,
Platinum ,, .	,,	$3{\cdot}0 \cdot 10^{-4}$	− 0·044	,,
Ferric oxide ,, .	,,	$3{\cdot}0 \cdot 10^{-4}$	+ 0·044	,,
Gold ,, .	,,	$2{\cdot}2 \cdot 10^{-4}$	− 0·032	Burton [4]
Platinum ,, .	,,	$2{\cdot}0 \cdot 10^{-4}$	− 0·030	,,
Silver ,, .	,,	$2{\cdot}4 \cdot 10^{-4}$	− 0·034	,,
Bismuth ,, .	,,	$1{\cdot}1 \cdot 10^{-4}$	+ 0·016	,,
Lead ,, .	,,	$1{\cdot}2 \cdot 10^{-4}$	+ 0·018	,,
Iron ,, .	,,	$1{\cdot}9 \cdot 10^{-4}$	+ 0·028	,,
Silver ,, .	,,	$3{\cdot}3 \cdot 10^{-4}$	− 0·048	Cotton & Mouton [5]
Oil (emulsion) ,, .	about 2μ	$3{\cdot}2 \cdot 10^{-4}$	− 0·046	Powis [6]

THE DEPENDENCE OF ELECTROKINETIC PROCESSES ON THE NATURE AND CONCENTRATION OF THE SOLUTES

In the following we shall deal for the present invariably with a solid body or a liquid not miscible with water, the wall-layer of which is charged negatively against the movable liquid.

The dependence of the electrokinetic phenomena upon the concentration and nature of the dissolved substances is very complicated. This probably depends upon the fact that, in accordance with the considerations on p. 250, ζ can depend in manifold ways upon the nature and concentration of the solutes. In Fig. 48, not only does the course of the potential curve itself change with a change in the composition of the solution; the thickness of the double layer changes as well; it may both increase and decrease, and not even the sign of this change is known *a priori*. For the present, therefore, we shall only distinguish between the *charging* and *discharging* action of dissolved substances. Here charging may denote increase of ζ or increase of thickness of the double layer; discharging, the reverse of these. In the case of non-electrolytes, a dielectric influence also may be present in the latter case. If, therefore, in the following all changes are for the present referred to changes in ζ, it is understood that the possibility has always to be reckoned with, that the thickness of the double layer also changes. The conclusions as to adsorption of the ions are drawn from exchange adsorption (cf. p. 212), which can only be done with great caution.

The most trustworthy measurements of the influence of electrolytes

[1] *loc. cit.* p. 241.
[2] Journ. Chem. Soc. **61**, 161 (1892).
[3] J. Amer. Chem. Soc. **26**, 1339 (1904). In this case an amount was deducted somewhat arbitrarily from the original value of u, which takes into account the disturbance due to gravity; see p. 1365 of the above paper.
[4] *loc. cit.* p. 244.
[5] Journ. d. Chim. Phys. **4**, 368 (1906).
[6] *loc. cit.* p. 244.

upon electrokinetic processes are those of Kruyt [1] and Freundlich and Rona [2] on stream-potentials with glass capillaries, and of Powis [3] on the kataphoresis of oil drops in aqueous solutions and on the electrosmosis of aqueous solutions against glass, the measurement of which could be combined in Powis's experimental arrangement with that of kataphoresis (cf. p. 246). Properly calculated,[4] the results of v. Elissafoff [5] in electrosmosis in glass and quartz capillaries agree with the above. The older experiments of Perrin [6] are to be regarded as only semi-quantitative.

It is generally observed with electrolytes having a univalent inorganic kation that ζ increases at first with increasing electrolyte concentration, reaches a maximum, and then decreases strongly and regularly. This is seen from Figs. 49 and 50. In Fig. 49 we have ζ values at the interface oil—water, derived from the kataphoretic experiments of Powis on oil drops; as abscissæ we have concentrations in millimols per litre, and not their cube roots as plotted by Powis. In Fig. 50 we have ζ values for the interface glass—water from measurements of stream-potentials by Kruyt in glass capillaries; here the concentrations are in micromols per litre. In both figures the potentials are given in volts. The maximum depends upon the adsorbability and valency of the anion; it is particularly strongly marked in the case of the OH'-ion, $Fe(CN)_6''''$-ion, and others. But it does not depend upon the adsorption of the anion being preferential as compared with that of the kation, for the influence of the kation makes itself felt from the start, and with strongly active kations, such as the multivalent ones, the maximum disappears and becomes merely a point of inflexion (cf. Fig. 49).

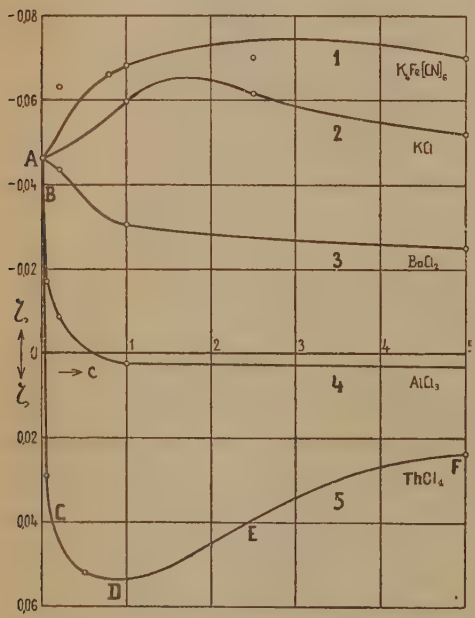


FIG. 49.—ζ, c Curves for the Interface Oil—Aqueous Solution.

With this *charging* action the question suggests itself whether the point may not be, that other anions besides the sluggish anion are able to pass into the wall and increase ζ because they increase ε. This is the more plausible since it is exactly the OH'-ion which is particularly able to charge, and in the case of glass it, as well as the H'-ion, is able to change ε, as appears from the experiments of Haber and Klemensiewicz. How far other ions have this power remains to be investigated; the picrate ion seems to be

[1] *loc. cit.* p. 246.
[2] *loc. cit.* p. 246.
[3] Zeitschr. f. physik. Chemie, **89**, 91 (1915).
[4] See *Kruyt*, Kolloidzeitschr. **22**, 93 (1918).
[5] *loc. cit.* p. 241.
[6] *loc. cit.* p. 241.

remarkable in this respect,[1] as also the anions of many organic sulphonic acids. This kind of entrance of ions of another kind into the framework of the solid wall corresponds to the behaviour discussed in the case of the adsorption of radio-active elements (cf. p. 220).

Another possibility is that the maximum does not arise directly from an alteration in ζ, but that an increase in the thickness of the wall-layer makes itself felt. This appears to be contradicted by the fact that the maximum extends to such high concentrations of electrolyte that, on account of the great concentration, we should rather expect a reduction in the thickness of the double layer.

If the electrolyte concentration further increases, the *discharging* effect of the kations is felt, the influence of the anions falls off. With many kations the discharge leads, at concentrations which are still small, through the zero value of ζ—the *iso-electric point*—to a positive charge, which then again decreases at still higher concentrations and again tends to become zero. In the case of other kations we only arrive at a smaller negative charge or at zero value, as the case may be. Fig. 50 shows how far the strong adsorbability of the kations makes itself felt; there is a much stronger lowering of the potential in the case of the $H^{\cdot}$-ion than in the case of the $K^{\cdot}$-ion, and a still stronger in the case of the organic kation of *p*-chloraniline. The experiments of v. Elissafoff and of Freundlich and Rona may further be cited, showing that the kations of the heavy metals, such as $Ag^{\cdot}$ and $Pb^{\cdot\cdot}$, have a stronger lowering effect than the light metals, and that basic dyes such as new fuchsine and crystal violet are particularly active and already reverse the charge of the capillaries at quite small concentrations.

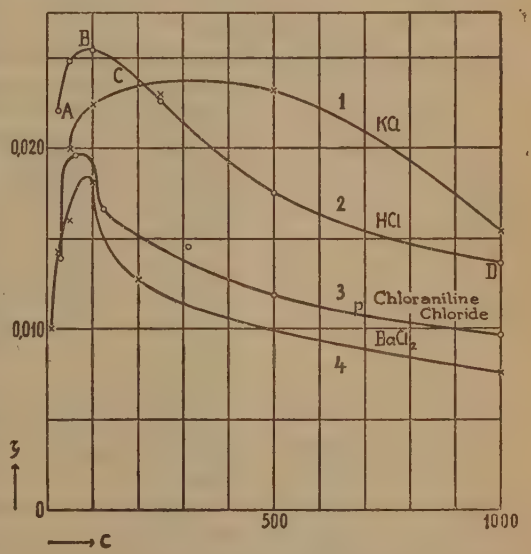


Fig. 50.—ζ, c Curves for the Interface Glass—Aqueous Solution.

Very remarkable are the great differences in the action of kations of different valency, as seen in Fig. 49. This shows how completely the maximum is obliterated in the case of $Al^{\cdot\cdot\cdot}$- and $Th^{\cdot\cdot\cdot\cdot}$-ions, and how strong is the positive charge. In Table 82 the action of $Th(NO_3)_4$ upon the electrosmosis in a quartz capillary is given after v. Elissafoff. *v* is the amount of liquid transferred electrosmotically in a given time in relative measure when pure water is taken as 50. The negative or positive sign tells us whether the liquid moves to the anode or to the kathode. The small concentration of 1·9 micromol per litre suffices to reach the isoelectric point.

[1] See *v. Elissafoff, loc. cit.* p. 241.

TABLE 82

Influence of $Th(NO_3)_4$ upon the Electrosmosis of Water in Quartz Capillaries

Concentration of Electrolyte (Micromols per Litre).	v.
0	− 50
0·36	− 27
1·0	− 2
1·9	0
3·8	+ 12

A concentration of $\frac{0.4}{1{,}000{,}000}$ mol per litre, that is, 0·2 mg. $Th(NO_3)_4 + 4H_2O$ per litre, suffices to reduce the amount of liquid transferred by 50 per cent. In the quantity of liquid used for the experiment, 0·0024 c.c., only 0·5 millionths of 1 mg. were contained; the surface in the capillary covered by the liquid was roughly 2 sq. cm. The great differences due to valency are particularly evident in the case of the kations of the base metals; with those of the noble metals and organic bases the stronger adsorption causes a greater lowering of the charge than is determined by valency alone. This great dependence upon valency, together with the small concentration necessary, permits of the determination by means of electrosmosis of the valency of a metal present in very small amount. The bivalency of radium was confirmed in this way.[1]

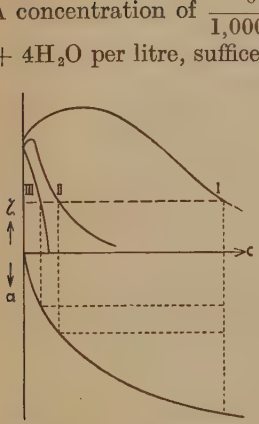


FIG. 51.—ζ, c Curves and Adsorption Isothermals.

This strong influence of valency does not depend upon the adsorbability of the ions increasing so greatly with their valency. Attention has already been drawn to the fact (cf. p. 203) that ions of different valency are frequently adsorbed equally strongly in equimolecular solution. This alone would actually suffice to explain the great influence of valency. The discussion later on of closely related phenomena (cf. p. 422) will show that the same depression of the charge is caused by *equivalent* amounts of the kation. Since the ζ, c curve and the adsorption curve relate to mols, it is those concentrations of kations of different valency which will bring about the same depression of charge and therefore of ζ,[2] for which the adsorbed amounts are inversely proportional to the valencies. If, therefore, in the case of a univalent kation, the amount adsorbed is unity for the molar concentration corresponding to a given ζ, this amount will be $\frac{1}{2}$ for a bivalent, $\frac{1}{3}$ for a tervalent kation, and so on. In Fig. 51, curves I, II, and III are the ζ, c curves of a uni-, bi-, and tervalent kation. The concentrations corresponding to equal depression of ζ are then found by drawing a parallel to

[1] *Freundlich* and *v. Elissafoff* (Physik. Zeitschr. **14**, 1052 (1913)).

[2] This is only true according to equation (3), p. 242, where the thickness δ of the double layer remains unchanged, which is not necessarily the case for a diffuse double layer.

the c axis and taking the abscissæ of the points where this parallel cuts the curves. If the values thus found are plotted against the amounts adsorbed of a uni-, bi-, and tervalent kation, that is, the values $1, \frac{1}{2}$, and $\frac{1}{3}$, as has been done in the lower part of Fig. 51, we see at once how well the points obtained fit an ordinary adsorption isothermal. This behaviour shows that the assumption of an approximately equal adsorption in equimolecular concentration is fairly well justified for these kations.

In the following Tables 83 and 84 are given the values of the concentrations which produce this equal depression of ζ, both for kataphoresis of oil drops and for electrosmosis in glass (Powis). The sequence of the figures

TABLE 83

Depression of ζ for the Interface Oil—Water by Kations of Different Valencies

Electrolyte.	Concentration (Millimols per Litre) which lowers ζ from about 0·046 volt, the value for Pure Water, to 0·037 volt.
KCl	24
BaCl . . .	0·45
$AlCl_3$ . . .	0·01
$ThCl_4$ . . .	0·005

TABLE 84

Depression of ζ of the Interface Glass—Water by Kations of Different Valencies

Electrolyte.	Concentration (Millimols per Litre) which lowers ζ from about 0·089 volt, the value for Pure Water, to about 0·039 volt.
KCl	25
BaCl . . .	0·87
$AlCl_3$ . . .	0·02
$ThCl_4$ . . .	0·015

in the two tables is very similar, although we are dealing with two very different interfaces; a sign that in the case of exchange-adsorption with which we are dealing here the specific properties of the non-aqueous phases and their influence upon the interface become insignificant provided that the sign of the charge of the wall-layer is the same.

There is a very decided difference between kations which cause a direct reversal of the charge of the wall-layer, and others which do not do so even in high concentrations. A reversal of charge is only possible in the case of very active kations, with which the isoelectric point is passed at very small concentrations. The ionic concentration is then still small enough, and hence the thickness of the double layer great enough, to allow of the

appearance of electrokinetic processes even in the region of a positive charge. In the second flexure of the ζ, c curve in the case of $Al^{\cdots}$- and $Th^{\cdots\cdot}$-ions in Fig. 49, and in the second zero value which is approached at higher concentrations no longer shown in the figure, the influence is felt not only of the discharging effect of the anion, but also of the reduction in thickness of the double layer and the increased conductivity, which again bring about the disappearance of electrokinesis. This value of the ionic concentration is reached for feebly active kations (such as those of the alkali metals) before the zero of ζ and the reversal of charge is reached. On the nature of the solid material also depends whether or not the charge is easily reversed. Amphoteric substances especially permit of an easy reversal. Thus, according to Bethe and Toropoff,[1] the charge of gelatine, proteins, and pig's-bladder is easily reversed by $H^{\cdot}$-ions, that of gypsum less easily ; that of collodion, charcoal, and wood not at all. Some experiments of J. Loeb[2] are particularly striking. Collodion membranes are not reversed in charge by $H^{\cdot}$-ions and multivalent kations, such as $Al^{\cdots}$, $Ce^{\cdots}$, $Th^{\cdots\cdot}$; but they are reversed, if the collodion membranes have been treated with a gelatine solution or with proteins (egg albumin, casein, etc.), which leave a fine coating upon the collodion membrane. According to Perrin, the charge on $CrCl_3$ may be easily reversed when used as a diaphragm material.

The ζ, c curve is so far from being simple that it does not appear to be advisable to attempt a mathematical treatment at present. Since, however, it is sometimes desired to calculate the depressent action of a given electrolyte concentration, it may be stated that the descending part of the curve, approximately about the portion CD in curve 2, Fig. 50, may usually be sufficiently well represented by an equation

$$\zeta = k \log \frac{\gamma}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which k and γ are constants, and c is the concentration of the electrolyte.

Experiments on positively charged layers are far less numerous. But from a few series of experiments combined with later results (cf. p. 420) it is quite certain that they behave quite symmetrically. In particular we know that the depressent action and reversal of charge depend in the same manner upon the adsorbability of the anions. Ferri- and ferro-cyanogen ions are hence particularly active. This influence of valency could be roughly estimated earlier[3] from the electrosmotic experiments of Perrin. Measurements by Burton[4] permit of more exact statements. He determined the kataphoretic speed of particles of a positive copper (more correctly copper oxide) sol by a macroscopic method. In the following table the concentrations are given which decrease the velocity by 20 per cent. (as a rule from $2{\cdot}5 \times 10^{-4}$ cm. per sec. for 1 volt per cm. in the pure sol to $2{\cdot}0 \times 10^{-4}$ cm. per sec. in one containing electrolyte).

It also appears from the measurements of Burton, that anions of equal valency and similar character in equimolecular solution depress about equally ; further, that the ζ, c curve begins with a maximum. Whether and in what way the maximum depends upon the nature of the kation has not yet been investigated.

A wall-layer charged positively by kations behaves throughout like one

[1] Zeitschr. f. physik. Chemie, **89**, 597 (1915).
[2] Journ. of Gen. Physiol. **2**, 255, 659 (1920).
[3] See the first (German) edition of this book, 1909, p. 238.
[4] Phil. Mag. (6), **17**, 583 (1909).

TABLE 85

Lowering of the Kataphoretic Speed of Particles of a Positive Copper Sol by Anions of Different Valencies. $t = 18°$

Electrolyte.	Concentration (Millimols per Litre) which reduced speed by 20 per cent.
KCl	115
K_2SO_4	49
$K_3Fe(CN)_6$ . .	2·2

originally charged positively; it is therefore to be expected that the descent DE in curve 5, Fig. 49, p. 258, for oil drops charged positively by $Th^{\cdot\cdot\cdot\cdot}$-ions will be strongly influenced by the adsorbability and valency of the anions.

In the measurement of electrosmosis and stream-potentials, in which the electrolyte solution investigated can be removed from the capillaries and rinsed out with water, the ease with which the original potential of the wall against pure water can be restored depends greatly upon the nature of the electrolyte used.[1] Thus, it is possible with salts having univalent inorganic kations in glass and quartz capillaries to regain the water value simply by repeated rinsing with cold water. It is increasingly difficult when strongly adsorbable kations of higher valency are present, so that with such electrolytes as $Th(NO_3)_4$ or crystal violet even long washing in hot water does not restore the original value, treatment with nitric acid and subsequent rinsing with water being necessary. This is connected with the fact that the concentration of these strongly active kations is so small that the kation is practically completely removed from the solution; the above-mentioned amount of $Th^{\cdot\cdot\cdot\cdot}$-ion (p. 259) is so small that, according to the results of other adsorption experiments (cf. p. 233), it could very well be taken up completely by the wall of the capillary. And it is well known how difficult it is to wash out when a solution has been practically exhausted by adsorption (cf. p. 193). On the other hand, with weakly active kations employed in comparatively large concentration, it is fairly easy to reach by rinsing a region of concentration which corresponds to a vanishingly small and no longer active amount adsorbed.

As regards the influence of *non-electrolytes*, up to the present capillary-active substances have been especially investigated; Grumbach[2] has followed the influence of alcohols and phenols upon the stream-potentials of a millimolar KCl solution in glass capillaries. The results are at present in various directions difficult to interpret. Grumbach makes use of the Helmholtz formula to represent them, thus neglecting the dielectric constant. According to the considerations on p. 253, this is not permissible. We might, however, suppose that the influence of the dielectric constant vanishes, since for comparatively dilute alcoholic solutions it does not sensibly differ from that of pure water. This appears equally doubtful, however, since, if it is a question of the adsorption of the organic substance, the concentrations in the boundary layer will be much greater, and the change in the

[1] See the measurements of *v. Elissafoff*, *loc. cit.* p. 241, which agree with the results of *Freundlich* and *Rona*.

[2] Ann. de chim. et de phys. (8), **24**, 433 (1911); Journ. d. phys. **2**, 283, 385 (1912).

dielectric constant may be too serious to be neglected. Grumbach assumes that adsorption has a strong influence on stream-potentials. The distinct change in the influence of the alcohols as we ascend the homologous series is in favour of this. It should, however, be remembered (cf. p. 211) that in the case of silicates, which distinctly adsorb by exchange, the adsorption of non-electrolytes is often very small, and that this is probably also true for glass. In any case, the assumption of an adsorption is not here so self-evident as to make quantitative proof superfluous. At present, the question of the influence of non-electrolytes upon electrokinetic processes is greatly in need of investigation and explanation.

Concentration Changes in Electrosmosis

The multiplicity of electrokinetic phenomena is not exhausted by the processes hitherto described. In the case of the diffuse double layer it is assumed that the charge of the movable layer of liquid depends upon an excess of one kind of ion, and that the sides of the double layer ζ are freely movable relatively to one another as ions are. Since now all ions contained in solutions are concerned in building up the boundary layer, the ions of the electrolyte present in the greatest concentration not being preferred, it may be expected that changes in concentration of the ions present in the solution will take place upon both sides of the diaphragm, and that these changes are connected by some law with the amount of liquid transported, also that the corresponding inverse phenomena will occur in the case of stream-potentials. Hittorf [1] was the first to describe changes of concentration of this kind in electrolysis through diaphragms. Bethe and Toropoff [2] have explained them to a large extent.

The phenomenon is as follows. Take a diaphragm, say of collodion or pig's-bladder, in a neutral dilute NaCl solution, and produce electrosmosis by means of electrodes lying on either side of the membrane. The wall-layer of this membrane is at the outset charged negatively. We then, after a short time, observe an alkaline reaction on the side of the membrane facing the + pole; an indicator, say rosolic acid, turns red close to the membrane. If the surface of the membrane lies in a vertical plane, we see from above a sharp red line appear close to the membrane. Together with this change in the reaction goes a decrease in the concentration of the electrolyte. On the negative side of the membrane, on the other hand, an acid reaction and increase in concentration are observed.

The following explanation given by Bethe and Toropoff has hitherto covered all observations. The wall-layer is negatively charged; the water moves toward the negative pole; more correctly stated, in the movable layer of liquid kations are present in excess, constituting the movable side of the double layer; these move towards the negative pole and take water with them, in part that which is bound to them as water of hydration.

As has just been said, all ions present in the solution, kations as well as anions, take part in determining the value of the potential ζ. The $H^{\cdot}$-ions always present in water will therefore take part in building up the double layer, and will be found as kation in the movable layer. In the negative wall-layer, on the other hand, are all anions in question, not only the anion of the electrolyte and the sluggish ion of the wall material, but also OH'-ions.

[1] Zeitschr. f. physik. Chemie, **39**, 9, 613 (1901); also *Cybulski* and *Dunin-Borkowski*, Anzeig. d. Akad. d. Wiss., Krakau, 1909, p. 660.

[2] Zeitschr. f. physik. Chemie, **88**, 688 (1914); **89**, 597 (1915).

Since in the narrow pores of the diaphragm a considerable proportion of the electric current goes through the fixed adherent layer of liquid, the anions will take a smaller part in the conduction of the current on account of their firm adherence ; they will behave as if they had a smaller transport number, while the unbound kations, which carry most of the current, behave as if they had a greater transport number. Hence, although the current in the diaphragm also passes through an aqueous solution, the solution in the diaphragm behaves differently from a solution present in greater amount ; hence the liquid in the diaphragm can be regarded as a second solvent, in which the transport numbers are different from those in an ordinary aqueous solution, and the conclusion is reached, as Nernst and Riesenfeld [1] have shown, that displacements of the concentrations of all ions present necessarily take place at the boundary surfaces of diaphragms. The diaphragm is, however, in so far different from such a solvent, that the transport numbers of the ions are not determined simply by the nature of the solvent but depend greatly upon the nature of the other ions present, the charge on the wall, etc.

Let m be the product of the transport number of the kation K of the electrolyte and its concentration, divided by the sum of these products for all ions which come into question; let n be the same number for the $H^{\cdot}$-ion, a for the anion A' of the electrolyte, and b for the OH'-ion, and the quantities m_1, n_1, a_1, and b_1 the corresponding values of these quantities in the diaphragm. As in the case of ordinary transport numbers,

$$m + n + a + b = m_1 + n_1 + a_1 + b_1 = 1 \quad . \quad . \quad . \quad . \quad (1)$$

If now an amount of electricity F ($= 96{,}540$ coulombs) pass through the diaphragm, we have the following changes upon the + pole side of the diaphragm :

Free Liquid.	Diaphragm.
+ Pole $+ m\mathrm{K}^{\cdot} \rightarrow$	$\rightarrow - m_1\mathrm{K}^{\cdot}$
+ Pole $+ n\mathrm{H}^{\cdot} \rightarrow$	$\rightarrow - n_1\mathrm{H}^{\cdot}$
+ Pole $- a\mathrm{A}' \leftarrow$	$\leftarrow + a_1\mathrm{A}'$
+ Pole $- b\mathrm{OH}' \leftarrow$	$\leftarrow + b_1\mathrm{OH}'$

. . . − Pole.

As balance B for the boundary of the diaphragm on the + side (vertical line) we get

$$\mathrm{B}_+ = (m - m_1)\mathrm{K}^{\cdot} + (n - n_1)\mathrm{H}^{\cdot} + (a_1 - a)\mathrm{A}' + (b_1 - b)\mathrm{OH}' \quad . \quad (2)$$

If we unite to molecules, we get

$$\left.\begin{aligned}\mathrm{B}_+ = {} & (a_1 - a)\mathrm{KA} + (n - n_1)\mathrm{H_2O} \\ & + [(m - m_1) - (a_1 - a)]\mathrm{K}^{\cdot} + [(b_1 - b) - (n - n_1)]\mathrm{OH}'\end{aligned}\right\} . \quad . \quad (3)$$

Now, according to (1)

$$(m - m_1) - (a_1 - a) = (b_1 - b) - (n - n_1)$$

hence

$$\mathrm{B}_+ = (a_1 - a)\mathrm{KA} + (n - n_1)\mathrm{H_2O} + [(b_1 - b) - (n - n_1)]\mathrm{KOH} \quad . \quad (4)$$

In the limiting case considered, a_1 and b_1 may be put $= 0$, m_1 and $n_1 = 1$; further, n and b are small in neutral solution, hence

$$\mathrm{B}_+ = -a\mathrm{KA} - (n_1 - n)\mathrm{H_2O} + (n_1 - n - b)\,\mathrm{KOH} \quad . \quad . \quad (5)$$

that is to say, there is reduction of electrolyte concentration, increase in OH'-ion concentration, and wandering of water towards the negative pole.

[1] Ann. d. Physik (4), **8**, 600 (1902).

Here Bethe and Toropoff quite rightly take into account a factor which has hitherto been neglected, namely, the hydration of the ions, as has already been briefly remarked. The argument just given only holds when the hydration of both ions is very small, or when that of anion and kation is equal. If the hydration of the anion greatly exceeds that of the kation in the free solution, the direction of wandering of the water may be reversed.

In corresponding fashion it may be deduced that on the negative side increase in electrolyte concentration and formation of acid will occur.

If the opposite case be considered, in which the anions are movable and the kations are held fast, the argument is the same, only the increase in neutral salt concentration and formation of acid now occur on the positive side.

All this agreed with experience. For gelatine diaphragms the last mentioned case was realized, when the wall-layer had been charged positively by multivalent kations.

In order to understand the phenomenon quantitatively, Bethe and Toropoff made use of a rather ill-defined quantity, *the disturbance time*, that is, the time required under given electrical conditions for a certain change of the indicator to be produced. Their measurements showed that it is independent of the thickness of the diaphragm, and that its dependence upon temperature is connected with the coefficient of viscosity and the dissociation constant of the water, as may be deduced for this case from the theory of electrosmosis (see p. 249).

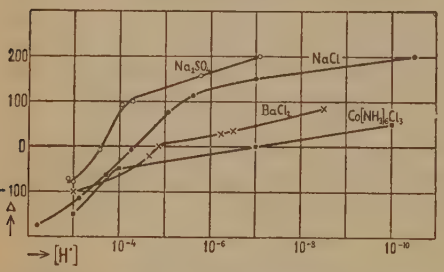


Fig. 52.—Electrosmotic Migration of Anions through a Membrane at various H· Concentrations.

Better defined is the change in concentration of the anion referred to unit amount of electricity passed, which is measured by determining analytically after a definite time the change in concentration in two compartments on either side of the membrane. If the composition of the solution is varied, ionic concentrations may be found for which no variations in concentration are observed. This point of indifference is, according to Bethe, the *true isoelectric point* at which the movable side of the double layer is not displaced, and at which therefore $\zeta = 0$. It lies close to the point at which the amount of water transported electrosmotically is zero. According to equation (5), p. 242, the latter has hitherto been taken as the isoelectric point. That the two do not strictly coincide depends, as Bethe correctly supposes, upon the fact just referred to that, in addition to the electrosmotic wandering, the movement of water due to the varying hydration of the ions must be taken into account.

For wall-layers such as chromated gelatine, whose charge is easily reversed by H·-ions or by multivalent ions, the dependence of the isoelectric point upon the nature and concentration of various ions can be followed. Fig. 52 gives a few examples for chromated gelatine; as abscissæ the H·-ion concentrations are taken, as ordinates the increase or decrease of the anion concentrations Δ (in relative measure) on the side of the membrane facing the negative pole. The solutions were so prepared that, for example, the neutral solution was 0·01 molar with respect to NaCl; in the acid

solution a part of the NaCl was replaced by the equivalent amount of HCl, in the alkaline by an equivalent amount of NaOH. For inorganic neutral salts such as KCl and NaCl the isoelectric point already lies fairly far in the acid region ; a sensible acid concentration is required to reverse the charge on the wall-layer ; for the rest, the curves for the two salts lie fairly close together, which entirely corresponds with the adsorption of these electrolytes and their other behaviour in electrokinetic processes. Multivalent kations charge positively, the isoelectric point is therefore reached at lower H·-ion concentrations, as may be seen from the curves for $BaCl_2$ and $Co(NH_3)_6Cl_3$. Conversely, multivalent and strongly adsorbable anions displace the isoelectric point towards the acid side, since they themselves tend to charge the wall-layer negatively. In this displacement, the charge maximum in the ζ, c curve (cf. p. 260), depending upon the valency and adsorbability of the anions, makes itself felt. The following table shows how great this displacement of the isoelectric point is numerically.

TABLE 86

Isoelectric Point of Chromated Gelatine in Solutions of Various Electrolytes

Electrolyte.	H·-ion Concentration at the Isoelectric Point.
Na_2SO_4 . . .	$10^{-3\cdot6}$
$Na_2C_2O_4$ . . .	10^{-4}
NaCl	$10^{-4\cdot3}$
KCl	$10^{-4\cdot3}$
$BaCl_2$	$10^{-4\cdot8}$
$Co(NH_3)_6Cl_3$ . .	$10^{-7\cdot0}$

The change of concentration is only considerable for dilute solutions of electrolytes, since only in their case is there a considerable proportion of those ions held fast in the wall-layer which have a relatively small mobility.

There can be no doubt that these phenomena are of the greatest importance in biological processes ; we are always dealing there with currents through membranes, and with the possibility of a disturbance of neutrality in the sense above described. The theory of general-excitation processes advanced by Bethe [1] upon the basis of these disturbances of neutrality can therefore beregarded as quite probable. He was able to show directly the disturbance in neutrality during the passage of a current in the case of the cells of the stem of *Tradescantia myrtifolia*.

Abnormal Osmosis, Electrostenolysis, Becquerel Phenomenon

A whole series of processes in capillaries and membranes may be referred to electrokinetic phenomena, or are connected therewith.

It may be regarded as certain that the osmotic phenomena in dilute electrolyte solutions are to be referred in large degree to electrosmotic

[1] Pflüger's Archiv, **163**, 147 (1916).

influences. The so-called *negative* or *abnormal osmoses*[1] in particular led forcibly to this conclusion. The success with which the theory of osmotic pressure had been applied to semi-permeable membranes in the case of solutions of sugar, etc., had allowed the fact to be overlooked that with membranes such as clay, collodion, pig's-bladder, parchment paper, which are not semi-permeable, and with solutions of electrolytes, a behaviour is met with which cannot by any means be readily explained by osmotic pressure. The most remarkable fact of this kind is the so-called negative osmosis, in which water does not pass from the dilute to the concentrated solution, or from the space containing pure water into that containing solution, but in the reverse direction. The idea has frequently been put forward, already by Th. Graham, that it may be a question of electrosmotic transport of liquid. In the place of a potential applied from outside, the *membrane potential* is then supposed to act; that is, a potential gradient between the two sides of the membrane. A condition for the existence of this potential is that the membrane separates two solutions of different concentrations, which is, of course, the necessary preliminary condition for osmosis. Such a membrane potential does not, however, suffice to make an electrosmotic transport of liquid possible. An electric current must also flow. This is not impossible. The mass of which the pore-walls of the membrane consist is usually not a perfect insulator, but is itself somewhat conducting in the case of many membranes, such as pig's-bladder, collodion, gelatine, etc. Local currents may therefore be formed, which flow in one direction through the pores, and in the opposite one through their walls, and these local currents may bring about an electrosmotic transference of liquid.[2]

While the investigators hitherto named only showed the fundamental possibility of explaining the osmotic behaviour of electrolytes electrosmotically, J. Loeb succeeded in proving the expected connexion experimentally.[3] The osmotic behaviour of the solutions in question was first investigated by means of collodion sacks. These were sometimes used without further preparation; generally they were rinsed out with a solution of gelatine (or of a protein) and afterwards washed with water, leaving a gelatin or protein film behind on the collodion. The electrolyte solution was poured into the collodion sack until it rose in a glass tube which projected into the solution. The sack was finally dipped into a beaker of pure water. The water generally forced its way into the solution, the liquid rose in the tube, the osmosis was positive; more rarely the tendency of the liquid to leave the sack, negative osmosis, gained the upper hand, which was seen by the liquid sinking in the tube. The rise of the liquid read after a certain time served as a measure of the osmotic activity.

The alkali salts with univalent inorganic anions, such as NaCl and KCl, showed first of all an increase of positive osmosis for small concentrations with increase in concentration, up to a maximum of about 4 millimols per litre, and then, with increase of concentration, a fall in osmosis with a

[1] They were first investigated by *Th. Graham* [Phil. Trans. Roy. Soc. London, **144**, 177 (1854)], after *Dutrochet* [Ann. de. chim. et de. phys. **60**, 337 (1835)] had already described the phenomenon. Among new investigations see *Girard* [Compt. rend. **146**, 927 (1908); **148**, 1047, 1186 (1909); **150**, 1446 (1910); **153**, 401 (1911); **159**, 99 (1914); *Bartell* [Journ. Amer. Chem. Soc. 36, 646 (1914)]; *Bartell* and *Hocker*, *ibid.* **38**, 1029, 1036 (1916); Frl. *Hamburger*, Zeitschr. f. physik. Chemie, **92**, 385 (1918).

[2] *Freundlich*, Kolloidzeitschr. **18**, 11 (1916).

[3] Journ. of Gen. Physiol. **1**, 717 (1919); **2**, 173 (1919); **2**, 255, 387, 563, 577, 659, 673 (1920).

subsequent rise from about 60 millimols onwards. The maximum appearing at low concentrations becomes decidedly steeper when we pass to anions of higher valency (sulphate, citrate, etc.), keeping the kation univalent (see Fig. 53A). This corresponds fully to the initial maximum in the ζ, c curve, as may be seen from a comparison of Figs. 53A and 53B. In Fig. 53A the logarithms of the concentrations are plotted against the osmotic rise h_0, in Fig. 53B the same function of the concentration is plotted against the electrosmotically transferred quantities of liquid; in the electrosmotic experiments, naturally, the membrane was in contact with the same solution inside and out.

We might conclude from this, with J. Loeb, that at low concentrations the electrosmosis indeed plays a predominant part; it is only the later rise, from 60 millimol per litre onwards, in a region of concentration in which electrosmosis becomes unimportant, that is to be regarded as the normal osmosis depending upon osmotic pressure. The maximum which is

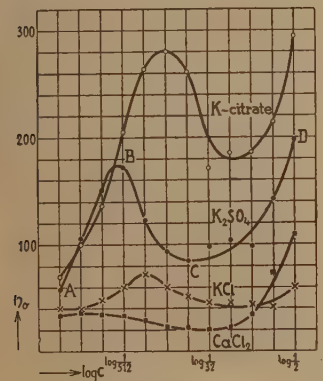


FIG. 53A.—Osmotic Transference of Liquid in various Salt Solutions.

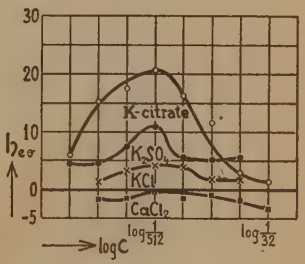


FIG. 53B.—Electrosmotic Transference of Liquid in various Salt Solutions.

attained depends upon the negative charging of the capillary wall caused by the anion and depending upon the ζ potential. The E.M.F. acting from outside, the membrane potential E_M, always acts in the same direction: inside, towards the electrolyte solution, the wall is negative; outside, towards pure water, positive; the positively charged water is therefore transferred from the outside to the inside (see Fig. 54). In this figure P represents a pore in the closely hatched membrane-wall, which lies between solvent and solution.

If we compare electrolytes with univalent anions and multivalent kations, we find with membranes of pure collodion at low concentrations an insignificant osmosis; only at higher concentrations, at which ordinary osmosis sets in, is a strong rise observed. With membranes, on the other hand, which had undergone preliminary treatment with gelatine or other substances, and therefore had their charge easily reversed, strong osmosis already occurred with ter- and quadrivalent kations at low concentrations. A comparison with electrosmosis showed that with pure collodion membranes the quantity of liquid transferred was slight, whereas with membranes containing gelatine the walls of the pores had their charge reversed and the liquid therefore wandered to the positive pole. Pure osmosis with multi-

valent kations would therefore be explained as follows : the charge on the capillaries of the membrane is reversed, the liquid is therefore negative. It moves in the direction of a positive osmosis from outside inwards, since the membrane potential E_M has also the opposite sign. The side facing the electrolyte solution is positive, that turned towards the water is negative.

Loeb was also able to detect negative osmosis,[1] particularly with membranes containing gelatine in dilute acid solutions, and in solutions of alkalis with bivalent kations. It corresponded to the descending portion BC of the curve *a*, Fig. 53 ; that is, the osmosis sinks so rapidly with increase in concentration that it becomes negative. This may be interpreted by supposing that the charge on the walls of the membrane capillaries is reversed, while the membrane potential E_M has still its original sign. The liquid is negatively charged, but the wall of the membrane on the electrolyte side is negative, that on the water side positive, the liquid therefore moves from the inside outwards. Both in the case of acids and of alkalis with kations of high valency it is possible, even probable, that the sign of the membrane potential E_M and of the electrokinetic potential ζ are in this direction.

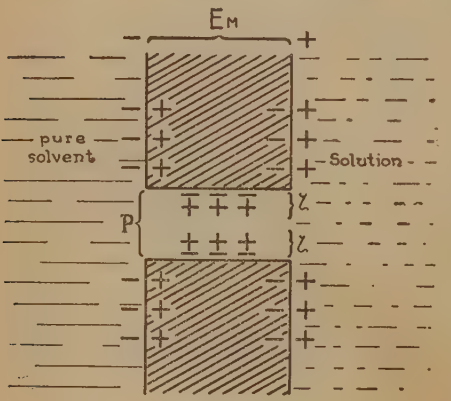


Fig. 54.

It is further noteworthy that the lyotropic series of anions and kations is unmistakable, in the sense that Li has less discharging power than Na, and this less than K. The maximum in the h_0, $\sqrt[3]{c}$ curve is therefore higher for LiCl than for NaCl, and for NaCl higher than for KCl. Conversely, Cl charges more strongly than Br, and this more strongly than I.[2]

Loeb proved in particular that the electrolytes in all these cases pass over into the pure water simply in proportion to their concentrations. Displacements in their concentrations cannot therefore be the cause of the complicated osmotic behaviour, but only the charge of the liquid and membrane. Nor could the difference in behaviour between a pure collodion membrane and one containing gelatine be referred to differences in their permeability ; this proved to be practically unchanged.

The least explicable part at present is the behaviour of the membrane potential E_M, and its connexion with ζ and ε.[3] In any case we shall have to take into account that, as in the above-mentioned experiments of Bethe and Toropoff, a displacement of the ionic concentration on both sides of the membrane will take place on account of the electrosmosis, and that this circumstance will influence the membrane potential ; we have an *electros-*

[1] Journ. of Gen. Physiol. **2**, 190 *et seq.* (1919).
[2] *J. Loeb*, Journ. of Gen. Physiol. **2**, 673 (1920).
[3] According to *Beutner* [Journ. Phys. Chem. **17**, 344 (1915)] the phase-boundary force developed on a copper ferrocyanide membrane is reversible towards univalent kations ; this reminds us of the phase-boundary force on glass, reversible towards H-ions.

motic polarization,[1] such as appears also when an electrosmotic liquid is forced through a membrane, which is bathed on both sides by the same solution.

It can hardly be doubted that, with the membranes investigated by Loeb, the unusual osmotic processes are to be referred to electrosmosis. Whether this is generally true for all membranes I should prefer to regard for the present as undecided. Hence the further possibility will be discussed later (cf. p. 698) that abnormal osmosis may also depend upon the velocity of imbibition.

Probably a number of natural phenomena are connected with negative osmosis ; for example, the secretion of liquid by glands, and the bleeding of plants. One can estimate that the potential differences occurring at the cell membranes are quite sufficient to account for the order of magnitude of the negative osmotic effects.[2] Since, however, we are always dealing with membranes capable of imbibition, the question still remains open, as has already been pointed out, that the abnormal osmosis may be caused by differences in velocity of imbibition.

According to Coehn,[3] *electrostenolysis*, discovered by Braun,[4] is also closely connected with electrosmosis. Under certain experimental conditions (sufficiently high potential, heavy metal solution, etc.), there was observed in the case of electrosmosis through suitable capillaries (e.g. cracks in glass) a deposition of metal on the side turned towards the positive pole, while on the other side development of gas took place. The end of the capillaries towards the positive pole will charge itself negatively, since, if the kations of the positively charged movable side of the double layer are torn away, the wall opposite to them remains negatively charged. Metal will be deposited upon this kathodic point, though in minute amount, since the quantities of electricity coming into play in electrosmosis are small, and the minute deposit will, as a rule, rapidly disappear, since as an intermediate conductor one side of the metallic particle will grow as rapidly as the other side dissolves. Under certain conditions, however, the metal will be able to grow further : firstly, when it is noble and hence difficultly soluble ; secondly, when a peroxide is formed on the anode ; thirdly, when the discharged anion, instead of dissolving the metal, oxidizes an " ous " salt in the solution to an " ic " salt. These are, as Coehn shows, actually the conditions which, according to Braun's experiments, must be fulfilled in order that electrostenolysis may take place.

The conditions under which Braun's experiments were made are distinctly different from those in most electrosmotic experiments ; in particular the electrolyte concentration and the potential gradients employed were much greater. Hence sparks are observed in the capillary, and the material nature of its wall plays a part which cannot at once be interpreted. Nevertheless, Coehn's explanation is to be preferred to the thermal one put forward in the first edition of this book, for Bethe and Toropoff [5] have observed an electrostenolytic separation of silver upon collodion membranes

[1] *Bethe* and *Toropoff*, Zeitschr. f. physik. Chemie, **89**, 634 (1915).

[2] *K. Stern*, Ber. d. deutsch. bot. Ges. **37**, 334 (1919) ; Zeitschr. f. Botanik, **11**, 561 (1920) : see also *Bredig*, V. internat. Kongresz f. angew. Chemie, Bd. IV, 646 (1903).

[3] Zeitschr. f. Elektrochemie, **4**, 501 (1898) ; Zeitschr. f. physik. Chemie, **25**, 651 (1898).

[4] Wied. Ann. **42**, 450 (1891) ; **44**, 473 (1891) ; further *H. N. Holmes*, J. Amer. Chem. Soc. **36**, 784 (1917).

[5] Zeitschr. f. physik. Chemie, **88**, 731 (1914).

under conditions which were entirely similar to those of ordinary electrosmosis.

Similar to ordinary electrostenolysis is the *Becquerel phenomenon*, which was first described by A. C. Becquerel [1] in the following form. A test-tube with a number of cracks (the phenomenon has also been observed with clay cylinders) is filled with a $Cu(NO_3)_2$ solution and dips into a Na_2S solution. At first CuS separates in the cracks; then, however, beautiful crystals of copper are formed in the cracks on the $Cu(NO_3)_2$ side, while on the other side a deep-yellow layer of solution containing polysulphide spreads out from the cracks. W. Ostwald [2] has explained the phenomenon as follows. CuS is semi-permeable; permeable to NO_3'-ions, impermeable to $Cu^{\cdot\cdot}$-ions. NO_3'-ions pass through the membrane and are neutralized by $Na^{\cdot}$-ions, which become free by the oxidation of the S''-ions to S_2''-ions. The negative charges set free discharge $Cu^{\cdot\cdot}$-ions to metallic copper. The mode of explanation may perhaps be somewhat modified. Without assuming semi-permeability, the membrane will certainly be oppositely charged by contact with the oxidizing and reducing solutions on the two sides. The membrane potential will produce an electrosmosis through the pores of the membrane, if the electric circuit is closed by means of the CuS itself as wall. As in the case of electrostenolysis, small amounts of deposited metal, which have separated upon the kathodic parts, can grow further if the conditions mentioned above (p. 271) are fulfilled. As a matter of fact, the reactions which produce the phenomena appear to conform to these conditions. The Becquerel phenomenon [3] would thus be an electrostenolysis by local currents, as negative osmosis in many cases is an electrosmosis by local currents. It may be mentioned that Becquerel also assumed a connexion with electrosmosis.

Hitherto we have been dealing with isothermal phenomena. In the case of the *thermosmosis* investigated by Lippmann [4] and Aubert,[5] a membrane such as collodion or pig's-bladder separates a hot from a cold liquid; in the case of water, for example, with quite a number of membranes (parchment, paper, viscose), an osmosis then occurs in the same direction as the temperature gradient. For other membranes (pig's-bladder, gelatine) it is opposed to the temperature gradient. The presence of a substance dissolved in the membrane is necessary for the appearance of the effect, for by means of careful washing-out it may be made to disappear, and by introducing a suitable substance (e.g. K-acetate) an otherwise inactive membrane (collodion) may be rendered capable of showing the effect. Probably the dissolved substance, which presumably must be capillary-active, causes a membrane potential dependent upon the temperature, which potential, as in the case of negative osmosis, leads to electrosmosis. In favour of this is, for instance, the fact that electrolytes, which diminish the electrokinetic potential ζ, also bring about disappearance of thermosmosis (cf. p. 277).

[1] Compt. rend. **64,** 919, 1211 (1867); **65,** 51, 720 (1867); **66,** 77, 245, 766, 1066 (1868); **67,** 1081 (1868); **71,** 197 (1870); **74,** 1310 (1872); **76,** 245 (1873); **78,** 1081 (1874); **79,** 82, 1281 (1874); **80,** 585 (1875); **82,** 354 (1876); **84,** 145 (1877); **85,** 169 (1877).

[2] Zeitschr. f. physik. Chemie, **6,** 71 (1890).

[3] For further experiments see *Giurgea*, Bulet. Societ. de Ştiinţe din Bucureşti, **21,** 192 (1912), cited from Chem. Zentralbl. I, 677 (1913); he attempts to explain upon the basis of this phenomenon the mineralogical occurrence of many reguline metallic crystals.

[4] Compt. rend. **145,** 104 (1907).

[5] Ann. de chim. et de phys. **26,** 145, 551 (1912).

Electrokinetic phenomena have found increasing technical application of recent years.[1] In particular, Count Schwerin, and the company founded by him (Gesellschaft für Elektroosmose m.b.H.), have proposed processes of this kind and also carried them out to a certain extent. Electrosmosis is especially applicable to the removal of liquid from porous masses. The usual method of working is to introduce the porous masses between perforated electrodes ; upon the passage of current the water passes out through the holes in the electrodes. It has been attempted to dry peat [2] in this manner ; the method is doubtless not yet cheap enough for practical application. The lixiviation of vegetable and animal products may also be rendered more effective by assisting the removal of the wash-water by electrosmosis [3] ; this process may be used for removing the bitter principle from lupins. In electrosmotic tanning [4] the hide hangs between perforated electrodes ; the washing-out is accelerated by electrosmosis, and the tan is introduced into the hide more rapidly by kataphoresis.

Kataphoresis serves especially for the removal of very finely divided and slowly settling substances from the liquid in which they are suspended. These finest particles have in the case of many plastic substances, such as clay, particularly valuable properties. Thus with impure clay the highly plastic fine particles may be suspended in aqueous solutions, thereby freed from coarser particles and impurities, and then thrown down kataphoretically.[5] With other substances, such as steatite and corundum, only the finest particles thus obtained are suitable for shaping plastically,[6] since only these sinter sufficiently far below the melting-point (see p. 105). For the purpose of kataphoresis a so-called electrosmotic machine is used [7] ; in this the electrode upon which the solid is to be separated is constructed in the form of a rotating drum, from which the deposited substance can be continuously removed by a scraper.[8]

Electrokinetic Phenomena in Non-Aqueous Liquids

For the electrokinetic potential difference set up in non-aqueous liquids, the rule put forward by Coehn [9] is found to be of importance, namely, that *a substance of higher dielectric constant in contact with a substance of lower dielectric constant charges itself positively towards the latter*. This rule relates to the phase-boundary forces ε, and not directly to the electrokinetic potential differences ζ. If it is none the less found to be true for the latter as well, this is due to the fact that if the variation in potential has the simple form of curve 1, Fig. 48, ζ and ε are symbatic to one another. This is particularly probable here, since in view of the comparatively large differences in the dielectric constants of the different liquids we are dealing with comparatively large differences in ε. Coehn and Raydt [10] measured the electrosmotic rise for a considerable number of organic liquids. The arrangement was such that the liquids under investigation only filled the capillary in which osmosis

[1] See also the article by *Supf* and *Prausnitz* in "Enzyklopaedie der techn. Chemie," VIII, p. 598, Berlin, 1920.
[2] German patents 124,509, 124,510, 128,085, 131,932, 150,069, 179,086.
[3] German patent 294,667.
[4] German patent 283,285.
[5] German patent 253,429.
[6] German patent 292,334.
[7] German patent 252,370.
[8] See the article by *Briggs* in the Second B.A. Report on the Progress of Colloid Chemistry. H.M. Stationery Office, London, 1916. [Trans.]
[9] Wied. Ann. **64**, 217 (1898).
[10] Ann. d. Physik (4), **30**, 777 (1909).

took place, while the capillaries which allowed the height of rise to be determined were always filled with the same liquid (usually methyl alcohol). The height of rise is therefore without further correction proportional to the pressure P reached (see formula (7), p. 243). They discovered the rule that the heights of rise h are proportional to the differences between the dielectric constants of the liquid and that of glass :

$$\frac{h}{h_0} = \frac{D - D_G}{D_0 - D_G} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here h and D are the electrosmotic height of rise and dielectric constant respectively of the liquid 1, h_0 and D_0 those of acetone, the liquid for comparison, D_G the dielectric constant of the glass of the osmotic capillary. Since the D_0 of acetone is not so well known as that of water, acetone was finally compared with water and all results referred to the latter. The following formula was thus obtained for the dielectric constant D_{E0} of any liquid :

$$D_{E0} = \frac{h}{h_W}(D_W - D_G) + D_G \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In the following table the values of D_{E0} found in this way by Coehn and Raydt are compared with those found in other ways.

TABLE 87

Calculation of Dielectric Constant from Electrosmosis

Liquid.	h.	D_{E0}.	D.
Water	+ 210	81	81
Nitrobenzene	+ 88·5	37·6	37·2
Acetonitrile	+ 106	43·6	36·4
Methyl alcohol	+ 80	34·5	34
Nitrotoluene	+ 51	24·2	27
Acetone	+ 60	27·5	26·5
Ethyl alcohol	+ 58	26·6	25·5
Propyl alcohol	+ 48	23·2	22·4
Isobutyl alcohol	+ 29·5	16·5	18·75
Benzaldehyde	+ 19	12·8	14
Pyridine	+ 14·4	11·3	12·4
Aniline	+ 7·8	8·8	7·3
Chloroform	− 1·67	5·4	5·18
Ethylene bromide	− 2·95	4·95	4·87
Benzene	− 8·9	2·8	2·4

The above-mentioned investigators conclude from equation (1) that the electrokinetic potential differences ζ are related to one another in the same way as are the differences in the dielectric constants. This would, however, as v. Smoluchowski [1] points out, only be true if Helmholtz' formula were valid for the electrokinetic processes, in which formula the dielectric constant is not taken into account (cf. p. 251). But if formula (7), p. 243, is used, then

$$\frac{h}{h_0} = \frac{\zeta D}{\zeta_0 D_0} = \frac{D - D_G}{D_0 - D_G}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

[1] *Graetz*, "Handbuch d. Elektrizität u. d. Magnetismus," II, p. 403 (1914).

that is, for substances of fairly high dielectric constant (for which $D_0 (= 6)$ may be neglected as compared with D), the values of ζ are not greatly different from one another.

It may further be emphasized that electrosmosis in these non-aqueous liquids is also very sensitive to impurities, as Coehn remarks with special reference to the nitro-compounds; this, again, is decidedly in favour of the view that we are dealing with an electrokinetic potential difference ζ and not with a phase-boundary force.

That the electrokinetic phenomena are particularly marked in liquids of high dielectric constant is a general experience to which Perrin[1] had already drawn attention.

In the kataphoresis of suspended particles the viscosity makes itself strongly felt as required by formula (8), p. 244. This is evident from the following table, which is taken from experiments by Burton,[2] and also gives information regarding the order of magnitude of the potential difference ζ in other liquids; the values correspond throughout to those observed for water. The suspended bodies were colloidally disperse metals.

Table 88

Influence of Viscosity in Kataphoresis in Non-aqueous Liquids

Solvent.	Suspended Substance.	D.	η.	u (cm. per sec. for 1 volt per cm.)	ζ (volts).
Methyl alcohol .	Lead . .	34	0·00612	$2{\cdot}2 \cdot 10^{-4}$	+ 0·046
,, ,, .	Bismuth .	34	0·00612	$1{\cdot}0 \cdot 10^{-4}$	+ 0·021
Ethyl alcohol . .	Lead . .	25·5	0·0123	$0{\cdot}45 \cdot 10^{-4}$	+ 0·024
,, ,, . .	Tin . . .	25·5	0·0123	$0{\cdot}36 \cdot 10^{-4}$	+ 0·019
,, ,, . .	Zinc . .	25·5	0·0123	$0{\cdot}28 \cdot 10^{-4}$	+ 0·015
Ethyl malonate .	Platinum .	10·7	0·0223	$0{\cdot}23 \cdot 10^{-4}$	− 0·054
,, ,, . .	Silver . .	10·7	0·0223	$0{\cdot}17 \cdot 10^{-4}$	− 0·040
,, ,, . .	Gold . .	10·7	0·0223	$0{\cdot}14 \cdot 10^{-4}$	− 0·033

Solutions in methyl alcohol have been much investigated.[3] The relationships are very similar to those in water. Solid substances, such as SiO_2, As_2S_3, PbI_2, have negative wall-layers; $CrCl_3$, $PbSO_4$ positive ones. Alcoholates charge negatively, acids reduce a negative charge, as do multivalent kations, while multivalent anions weaken a positive charge.

It is noteworthy that, according to Ascoli,[4] liquid NH_3 with Al_2O_3 diaphragms shows electrosmosis in accordance with its fairly high dielectric constant (22), the liquid being negatively charged. If Na is dissolved in the liquid to the well-known blue solution, the liquid wanders still more strongly to the positive pole.

Electrokinetic Potential Difference and Phase-boundary Force at the Interface Liquid—Liquid

The kataphoresis of oil-drops in aqueous solutions is so completely similar to that of the kataphoresis of solid particles that it may be straight-

[1] *loc. cit.* p. 241. [2] Phil. Mag. (6), **11**, 441 (1906).
[3] *Baudouin*, Compt. rend. **138**, 898 (1904).
[4] Compt. rend. **137**, 1253 (1903).

way included in the above discussion. But something more must be said here about the phase-boundary forces at liquid interfaces and their possible connexion with the electrokinetic potential difference.

Such phase-boundary forces have been investigated in recent years by Beutner [1] and Baur.[2] The experimental arrangement may be of very various kinds. One used by Beutner permits of quick measurement against different solutions. An **S**-shaped glass tube opens at its upper end into a normal electrode, its lower **U**-shaped part contains the liquid not miscible with water. This part dips into a beaker, which contains the aqueous electrolyte solution of variable concentration and composition, and has a second normal electrode dipping into it. Under what conditions appreciable differences of potential appear may be illustrated from the measurements of Baur and Kronmann.[2] They used amyl alcohol shaken with KCl as non-aqueous phase; as the first aqueous phase a KCl solution; as second an equally concentrated KCl solution containing in addition an electrolyte with organic kation or anion; strychnine nitrate or potassium picrate were principally employed. Without such electrolytes, with different inorganic electrolytes only upon the two sides, the E.M.F. was small. It assumed considerable values—up to 150 millivolts and more—when the organic ions were added. The drop of potential at the amyl alcohol boundary depended both upon the anion and upon the kation, in the opposite sense in the two cases: the picrate ion caused with increasing concentration an increase in the potential difference in the sense that the side of the double layer towards the amyl alcohol became more strongly negative; the strychnine ion in the sense that it became more positive. Beutner's experiments also confirm these results to a great extent; they show, further, that these potential differences are usually set up quickly and reversibly, and that when the charge is produced by a kation the nature of the anion is of little importance, and vice versa. It should also be mentioned that other capillary-active substances, such as thiocyanates, amines, salicylic acid, mercuric chloride, produced the effect. An influence of the valency of inorganic anions and kations is not distinctly traceable.

Beutner refers these phase-boundary forces to the distribution of the ions between the two phases, for which the law found by Nernst and Haber (cf. p. 256) holds; Baur prefers the view of an adsorption P.D., that is, a P.D. which depends sensibly only upon the distribution of the ions within the aqueous phase. From the standpoint here maintained we are dealing in every case of such transverse measurements with a phase-boundary force ε, not with an electrokinetic P.D. ζ. If the similarity between the behaviour of the E.M.F. of these combinations and that of the drops of the corresponding liquid in kataphoresis in the same solutions is great, this would naturally tell in favour of Baur's view, but not necessarily conflict with Beutner's view; for the possibility has already often been mentioned (cf. p. 273) that when the course of the potential curve is simple, ζ and ε may be to a great extent symbatic, even without the greater part of the potential gradient falling in the aqueous liquid. A comparison of the two

[1] "Die Entstehung elektrischer Ströme in lebenden Geweben." Stuttgart, 1920. Further, Zeitschr. für Elektrochemie, **19,** 319, 467 (1913); **24,** 94 (1917); Zeitschr. f. physik. Chemie, **87,** 385 (1914); J. Amer. Chem. Soc. **36,** 2045 (1914); Elektrochem. Zeitschr. **22,** 177 (1915); *J. Loeb* and *Beutner,* Biochem. Zeitschr. **51,** 288 (1913); **59,** 195 (1914).

[2] Zeitschr. f. Elektrochemie, **19,** 590 (1913); **24,** 100 (1917); *Baur* and *Kronmann,* Zeitschr. f. physik. Chemie, **92,** 81 (1916).

phenomena, similar to the one instituted for glass by Freundlich and Rona (cf. p. 251), would doubtless be worth while.[1] It is, however, not quite easy to carry out; for the phase-boundary forces become considerable at high electrolyte concentrations, at which the particles transferred kataphoretically are to a great extent discharged. That the phase-boundary forces make themselves felt at higher electrolyte concentrations, at which kataphoresis disappears, does not, of course, contradict the supposition of an adsorption P.D.; a gradient of potential caused by adsorption of ions and present in the water may certainly occur, only the thickness of this double layer, in accordance with the theory of the diffuse double layer (cf. p. 254), is so small that it no longer makes itself felt in electrokinetic processes.

A certain similarity between these phase-boundary forces and the electrokinetic P.D.'s is undoubtedly present, as Beutner [2] indeed remarks: dependence upon kation as well as anion, positive charge with increasing kationic concentration, negative with increasing anionic, small influence of the anions upon the positive charging, and of the kations upon the negative. As we have said, it remains an open question whether this depends simply upon a symbasis with ζ on the part of the P.D. ε, which is determined by ionic distribution, or whether it depends upon a P.D. due to adsorption.

The dependence of the phase-boundary force upon the concentration of the specially active ion does not, according to available data obtained with considerable electrolyte concentrations, take so complicated a course as the ζ, c curve frequently does (cf. p. 257), but may be represented by a logarithmic function of the electrolyte concentration.

Beutner [3] and Baur [4] both remark quite truly that phase-boundary forces of the kind realized by them at the boundary of non-aqueous phases in presence of capillary-active ions are frequently of importance for biological phenomena. Thus, according to Baur we may arrive upon the basis of such potentials at the order of magnitude of the effects exhibited by the electric organs of various animals, and Beutner shows that the considerable P.D.'s at plant and animal membranes, which depend greatly upon the concentration of simple inorganic salts such as NaCl, may be imitated if, say, salicylic aldehyde saturated with salicylic acid—hence an organic liquid containing a capillary-active substance—is made to border on an aqueous solution of the inorganic salt. Such cases, in which substances contained or produced in the membrane are important for the formation of P.D.'s, were already met with earlier (e.g. under thermosmosis, p. 272), and are probably of outstanding importance for biological phenomena.

Electrokinetic P.D. and Phase-boundary Force at the Interface Liquid—Gas

In electrokinetic phenomena we have hitherto been dealing with the case in which one side of the electrical double layer was in a film of liquid

[1] Experiments by *Gyemant* [Zeitschr. f. physik. Chemie, **100**, 74 (1922)] have shown that here also the potentials ε and ζ are entirely independent of one another. The ε potential, in accordance with the results of *Beutner*, depends upon the distribution of the electrolyte between the two liquids; for the ζ potential, on the other hand, the regularities mentioned upon p. 257 *et seq.* hold.

[2] Zeitschr. f. Elektrochemie, **19**, 476 (1913).

[3] *J. Loeb* and *Beutner*, Biochem. Zeitschr, **41**, 1 (1912); **44**, 303 (1912); **51**, 300 (1913); *Beutner, ibid.* **47**, 73 (1912). A number of examples are given in *Beutner's* monograph cited on p. 276.

[4] *loc. cit.* p. 276.

attached to a solid wall or to a second non-miscible liquid. The case of the solid wall was much more prominent, but the kataphoresis of oil-drops took place under exactly the same laws which hold, say, for stream-potentials in glass capillaries (cf. p. 261). Now, it is fundamentally of great importance that the layer of liquid which is adjacent to a gas has similar properties to that adhering to a solid or liquid wall, and that between it and the remaining liquid a P.D. ζ exists, which is in no way essentially different from the quantity ζ hitherto discussed. Quincke [1] already observed that gas-bubbles in a liquid wander kataphoretically, and the detailed investigation of these processes by McTaggart [2] permits of the assertion just made.

Of the various arrangements used by McTaggart, one only will be shortly described (see Fig. 55). The stoppers AA ground into the tube B carry at their ends platinum electrodes C C. A pulley D allows the tube to be rotated at a uniform speed, in order that the gas-bubble which is introduced through an opening E, which may afterwards be closed, shall remain in the middle of the tube. By means of a stop-watch the time is determined which the bubble takes to move over a certain distance which could be read off on a scale.

First of all the physical requirements of equation (8), p. 244, proved

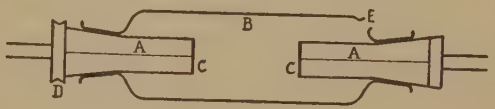


Fig. 55.

to be fulfilled. The velocity of motion was proportional to the potential gradient and was independent of the size of the bubble; thus the time required to cover a certain distance varied without systematic error between 10·0 and 10·9 secs., while the diameter of the bubble varied from 0·06 to 0·16 mm.

The gases air, hydrogen, and oxygen all wandered to the anode; hence their wall-layer is negatively charged. It is therefore a very general fact that the extreme layer of water against any other phase, whether gas, liquid, or solid of very various descriptions such as noble metals, glass, and fibres, is preferentially negatively charged.

The absolute magnitude of the kataphoretic velocity u corresponds entirely to that observed with solid and liquid particles; it amounted, for a potential gradient of 1 volt per centimetre,

for air to $4{\cdot}1 \times 10^{-4}$ cm. per sec.
for hydrogen to $4{\cdot}2 \times 10^{-4}$ cm. per sec.

Oxygen was not sensibly different. We may compare with this the values given in Table 81, p. 257.

Electrolytes again lower the velocity and the potential ζ. The latter quantities sank for acids such as HCl and HNO_3 to zero, without a reversal of charge occurring, as was also observed for electrosmosis and stream-potentials in the case of glass and other materials. Particularly strong was the discharging action of multivalent kations; with ter- and quadrivalent ions ($Al^{\cdots}$, $La^{\cdots}$, $Zr^{\cdots\cdot}$, $Th^{\cdots\cdot}$) a pronounced reversal of charge was

[1] *loc. cit.* p. 241.
[2] Phil. Mag. (6), **27**, 297 (1914); **28**, 367 (1914).

attained. The following table gives the values found with $Th(NO_3)_4$. If it be compared with Table 82, we see that in the case of air the reversal

TABLE 89[1]

Influence of $Th(NO_3)_4$ upon the Kataphoresis of Air Bubbles

Electrolyte Concentration (Micromol per L.).	Velocity of the Bubble (in a relative Measure).
0·017	− 0·040
0·17	+ 0·013
1·7	+ 0·018
3·5	+ 0·021
7·0	+ 0·025

of charge takes place at a concentration of about 0·13 micromol per litre, while for the electrosmotic experiments in quartz capillaries it took place at about 1·9 micromols per litre. If we take into account the fact that in the quartz capillary the size of the active interfacial surface was about fifty times larger than the probable surface of McTaggart's bubble, we see that the influence of the thorium salts is similar in order of magnitude.

If, conversely, salts with multivalent anions (such as potassium ferro- and ferricyanide) were added to a solution containing $Th(NO_3)_4$, in which the bubble was positively charged, the latter was discharged and then acquired a strong negative charge, in accordance with the activity, often referred to, of these multivalent anions.

The influence of organic substances also reappeared in a manner similar to that described by Grumbach [2] for stream-potentials. Alcohols lowered the kataphoretic velocity of the gas-bubble, and the effect increased with their capillary activity; that is to say, the Traube rule was distinctly followed.

Some points still require explanation. If the liquid was not saturated with air, the gas-bubbles decreased in volume. In the case of solutions their migration velocity also often decreased noticeably. Thus, in a very dilute $Th(NO_3)_4$ solution, in which the bubble was originally negative, the velocity was observed to decrease and finally to change its sign, that is, it behaved as if the solution had become more concentrated. It would almost appear as if the amount originally adsorbed does not decrease in proportion as the bubble diminishes in size, but that the same amount on the smaller surface produces a greater effect as regards discharge and reversal of charge. This reminds us of the phenomenon in glass and quartz capillaries noted in the experiments of v. Elissafoff, that it is precisely with such salts as $Th(NO_3)_4$ that the capillary is very difficult to wash out (cf. p. 263). The fact would be immediately comprehensible if practically all the salt were adsorbed on the boundary surface.

The opposite was observed in alcoholic solutions. The rate of motion of the diminishing bubble increased and passed over into that for pure water. This is still difficult to explain, the more so since the whole action of organic substances is not completely clear. Perhaps the following

[1] Recalculated from the table given by *McTaggart* on p. 305 of his paper [Phil. Mag. **27** (1914)].

[2] *loc. cit.* p. 263.

interpretation may meet the case. In the diminution of the bubble not only is the diameter of the diffuse double layer diminished, but also its thickness, since the charge becomes spatially more dense and this diminishes the thickness of the double layer (cf. p. 254). If, however, the thickness becomes small with the increased charge, capillary-active non-electrolytes will be thrust out, just as their action disappears in the strongly charged branches of the electro-capillary curve of mercury (cf. p. 294).

The fact that inorganic salts must here be assumed to be positively adsorbed does not appear to be in agreement with earlier experience. At all other interfaces, such as those of charcoal, glass, and oil, this assumption is justified, since they are actually positively adsorbed and lower the interfacial tension (cf. p. 90). At the interface water—air, however, they almost always raise the surface tension, and hence should be negatively adsorbed. This rise of σ refers, of course, to much more concentrated solutions. In such dilutions as come into question here a change in the surface tension cannot be established. It is not impossible that in this range of concentration the surface tension may be lowered by these electrolytes and positive adsorption take place, in accordance with the very general experience, that the first small amount of a foreign substance always causes a lowering of σ. The first gentle rise of the σ, c curve for inorganic salt solutions would thus be the region of a minimum in the σ, c curve, only that this minimum, since it is very slight, cannot be measured.

In any case it appears from these experiments that an electrical double layer is to be assumed at the interface liquid—gas, both sides of which lie in the liquid, and which is completely similar to the double layers acting at solid and liquid interfaces. The experiments further confirm the fact that in adsorption specific attraction by a solid, liquid, or gaseous adsorbent vanishes completely, and the adsorbed substances are characteristically different only as regards the work required to bring them from the interior to the boundary surface of the solvent, which work is done against the attraction of the molecules of the latter (cf. p. 188).

The question now arises as to how far we are able to prove the existence at the liquid—gas interface, in addition to the electrokinetic P.D. ζ, of a phase-boundary force ε, as is detected by transverse measurements. Attempts to measure such a force have been made. Thus Kenrick [1] compared the cells

1. N-KCl Solution | Liquid A | Air | Liquid B | N-KCl ; and
2. N-KCl | Liquid A | Liquid B | N-KCl,

the difference between which gives the P.D. Liquid A | Air | Liquid B. The E.M.F. of the cell was measured as follows :—The liquid A trickled out of a beaker down the walls of a narrow tube, through the centre of which the liquid B also dropped from a beaker. The object was to impart to B the same potential as that of the surrounding air, so that really only the P.D. between A and the air was measured. Normal electrodes, dipping into the beakers containing A and B, were connected to the quadrants of an electrometer. The experiments are perhaps open to the objection that ballo-electric actions, as discussed in the next section, may take effect. In any case, distinct P.D.'s are observed, if Solution A contains, in addition to KCl, also capillary-active substances such as acetic acid, butyric acid,

[1] Zeitschr. f. physik. Chemie, **19**, 625 (1896).

and camphor, and a parallelism between capillary activity and magnitude of the observed P.D. is present. The P.D. was not sensibly dependent upon the nature of the gas.[1]

Ballo-Electric Phenomena

It appears to me to be decided by recent experimental work that waterfall- or ballo-electricity[2] is closely connected with electrokinetic processes, as was suggested in the first edition of this book. Waterfall-electricity is observed when a liquid is formed into as fine a spray as possible. Fig. 56 shows a practicable experimental arrangement.[3] The liquid to be investigated, which is contained in the well-insulated vessel A, is driven by means of a sprayer ("atomizer") Z against the electrode E; this, as well as the liquid in the vessel, is connected to an electrometer. Pure water charges itself positively under these circumstances; the corresponding negative charge is contained in the gas-space. The development of electricity upon the bursting of gas-bubbles in a liquid, chiefly investigated by Coehn and Mozer,[4] is also to be regarded as ballo-electric.

It was already assumed earlier[5] that the electrical double layer, the destruction of which conditions the phenomenon, is not at the interface liquid — gas, but completely within the liquid. Lenard[6] arrived at the same conclusion, chiefly on account of the following fact. Ballo-electricity does not appear when liquid merely rubs on gas, as when a rapid jet of liquid passes through the air; nor does it appear when a liquid surface disappears without spray. The "atomizing" of the outermost liquid layer by a sufficiently large, tangential force is absolutely necessary. With water the ballo-electricity is to a great extent independent of the nature of the gas[7]—H_2, O_2, N_2, air, CH_4, and CO were examined. The small differences found may be referred to the different densities of the gases, since in a less dense gas the "atomizing" which takes place under the same conditions is less intense.

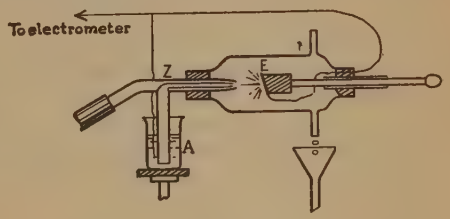


Fig. 56.

[1] A further observation of *Kenrick's* becomes intelligible after what was said earlier on p. 50. With butyric acid and ethyl benzoate solutions a distinct P.D. existed when the active solution was measured while dropping against a trickle of the same solution, which was not the case with other solutions. The direction was as if the dropping solution had not had time to establish its potential difference. Hence here also a dynamic surface tension must be distinguished from the static, and evidently a certain time is required for the adsorption equilibrium to be set up.

[2] First investigated by *Lenard* [Wied. Ann. **46,** 584 (1892)]; for further literature see *Kähler,* Ann. d. Physik (4) **12,** 1119 (1903).

[3] According to *Christiansen* [Ann. d. Physik (4) **40,** 122 (1913)].

[4] Ann. d. Physik (4), **43,** 1048 (1914).

[5] First (German) edition of this book, p. 258 (1909).

[6] Sitzungsber. d. Heidelb. Akad. 1914, 28 Abt. p. 23 *et seq.*

[7] This statement is probably more trustworthy than earlier statements by *J. J. Thomson* [Phil. Mag. (5), **37,** 241 (1894)], who believed that he had observed a considerable effect of the nature of the gas also in the case of water. With mercury as sprayed liquid greater differences are apparently present [see *A. Becker,* Ann. d. Physik (4), **29,** 909 (1909)]; perhaps the stronger adsorption of the gas on the mercury surface plays a part.

The production of ballo-electricity, therefore, recalls to some degree stream-potentials ; tangentially acting mechanical forces destroy the double layer lying in the liquid, only the force does not, as in the case of stream-potentials, act on the movable inner portion of the double layer lying within the liquid, but on the outer portion, which generally adheres firmly to the wall. Since at the boundary between liquid and gas both sides are easily movable, not merely a displacement but an actual destruction of the double layer takes place, and carriers of electricity from both sides of the layer can get into the gas. This leads to the result that the dependence upon the nature and concentration of dissolved substances is distinctly more complicated than in the other electrokinetic phenomena. If, for example, a neutral point is found, we cannot say that the double-layer potential ζ is then zero, but only that under the experimental conditions an equal number of positive and negative carriers can escape into the air and so leave the liquid neutral. Hence the degree of force used in producing the spray may alter the position of the neutral point, as is actually the case.[1]

None the less, the relationship to other electrokinetic phenomena is unmistakable. Water acquires a positive charge, that is to say, the side of the double layer toward the gas is negative as in the experiments of McTaggart (cf. p. 278). With different liquids the effect is in general greater, the greater the dielectric constant, as is especially to be seen from the experiments of Coehn and Mozer (see p. 281). This is a confirmation of Coehn's rule (see p. 273), although not in the sense in which it was originally intended, since the double layer lies entirely within the liquid.

We must again call to mind the connexion between ζ and ε, to which attention was drawn on p. 273, which exists when the potential curve has a simple course. From what was said on p. 274, the conclusion may probably be drawn that the active potential difference varies but little from liquid to liquid.

As regards ballo-electricity with aqueous solutions,[2] inorganic electrolytes tend to discharge at first ; a neutral point is already reached at low concentrations. The preponderating influence of the kations in this discharging entirely corresponds to their behaviour in other electrokinetic phenomena ; $H^{\cdot}$-ion already leads to the neutral point in lower concentration than other univalent inorganic kations. Organic kations of high molecular weight, such as those of the basic dyes, act surprisingly strongly. With fuchsine, for example, a neutral point is reached at a concentration of 0·25 micromol per litre ; at 2·5 micromols a decided reversal of charge occurs, that is, the water becomes negatively charged.[3] The strong action of basic dyes upon electrosmosis may be recalled ; 50 micromols of crystal violet per litre discharge a glass capillary down to the isoelectric point, greater concentrations charge the layer adhering to the glass positively.[4] The valency of the kations does not make itself plainly felt, according to Christiansen, a is otherwise the case in electrokinetic processes. Perhaps their influence upon the P.D. ζ is masked by an oppositely directed influence of these multivalent kations upon the number of gas ions formed. Acid dyes (O. Rohde)

[1] *Lenard*, Sitzungsber. d. Heidelb. Akad. 1914, 29 Abt. p. 12.

[2] See on this point *O. Rohde* [Ann. d. Physik (4), **19**, 935 (1906)], *Coehn* and *Mozer* (*loc. cit.* p. 281), and especially *Christiansen* [Ann. d. Physik (4), **40**, 107, 233 (1913); **51**, 530 (1916); **59**, 95 (1919)].

[3] *O. Rohde, loc. cit.* under [1].

[4] *Freundlich* and *Rona, loc. cit.* p. 251.

and hydroxyl ions (Christiansen) increase the negative charge of the external layer, and therefore the positive charge of the water.

The superposition of the two influences just mentioned, the change in ζ and the number of carriers of electricity formed, should always be borne in mind, especially in the case of organic electrolytes and non-electrolytes, for it is not probable that their ballo-electric action, in part surprisingly powerful, is to be ascribed to a change produced by them in ζ alone; probably an increase in the number of carriers of electricity in the gas space is of particular importance. Eve [1] states that alcohol and allied substances allow more carriers to be formed than does water. At present there is no possibility of distinguishing the two influences.

Substances which charge the boundary surface more strongly negatively, the water therefore positively, are the alcohols, fatty acids, and other substances. Christiansen calls them *autokataballic*. *Autoanaballic*, on the other hand, are such substances as not only discharge the boundary surface, but also recharge it positively, the water therefore becoming negative. To these belong, for example, aniline, quinine, and the chloracetic acids. Very well marked, also, is the fact that non-electrolytes only act moderately strongly by themselves, but much more strongly in conjunction with an otherwise feebly active electrolyte. Thus, for example, ethyl alcohol in 1-molar solution by itself has, according to Christiansen, a ballo-electric action of 0·9 (in arbitrary units), KCl in 1-molar solution one of 0·1; equal volumes of the two solutions mixed, on the other hand, one of 7·0. Alcohol is thus *hyperkataballic*. As *hyperanaballic* substances the chloracetic acids may be named. Only by the influence on the double layer being superimposed upon changes in the nature and number of the carriers can the fact be explained that many substances, such as aniline, are autoanaballic alone, but hyperkataballic when associated with an electrolyte.

The ballo-electric power of alcohols, fatty acids, and amines increases greatly in ascending the homologous series. Traube's rule thus reappears. That the rise is not so regular as usual is again to be interpreted as a result of the superposition of two influences. The contrast between an aballic, capillary-inactive salt, such as potassium acetate or ethylamine acetate, and the strongly ballo-electric solution which contains an excess of the capillary-active substances, acetic acid or ethylamine, is very distinct. Experiments such as those performed by Windisch and Dietrich (p. 61) could be repeated throughout by ballo-electric means. In short, these phenomena may be actually regarded as a proof that according to their capillary activity substances are adsorbed at the boundary surface liquid —gas, and that the organic acids and amines, which are dissociated slightly, or not at all, are much more capillary-active than their ions (cf. p. 73). The extremely strong influence of small amounts of substance is very striking. The ballo-electricity of water increased in the experiments of Christiansen by more than 100 per cent. when the water had been previously in contact with a small amount of filter-paper, silk, old linen, or an oil. When means have been found to control these processes better, they should find wide application in micro-chemistry.

As regards the carriers of electricity appearing in waterfall-electricity, they are, as one might suppose, very various and frequently very large. According to a rediscussion of the measurements of Aselmann [2] by Lenard [3]

[1] Phil. Mag. (6), **14**, 382 (1907). [2] Ann. d. Physik (4), **19**, 960 (1906).
[3] Sitzungsber. d. Heidelb. Akad. 1914, Ab. 29, p. 16.

the negative carriers in the case of ballo-electric experiments with water and NaCl solutions are of about molecular dimensions ; the positive, which only appear in the case of NaCl solutions, contain Na, and the smallest are not less than 8 $\mu\mu$ in diameter, the majority of 15 $\mu\mu$ diameter, being thus minute drops with an excess of Na ions. Lenard rightly hopes that a more exact analysis of these carriers will throw much light upon the structure of the surface-layer of various solutions.

Frictional Electricity

There is much to be said in favour of the view that in frictional electricity the sign of the charge produced is related to the P.D. which determines electrokinetic processes. The fact that the contrast between basic and acid substances appears again here, and, further, the decided activity of substances of high molecular weight, such as the organic colouring matters and alkaloids, point in the same direction.

As example we may take first the experiments of Knoblauch.[1] He used plates of the one solid, upon which the other was spread as a powder. By turning the plate he allowed the powder to fall off ; it either fell off by itself, or was caused to fall off by tapping. The charge observed on the electrometer was practically the same in the two cases.

His results may be summarized as follows :—Plates of substances which were neither appreciably basic nor acidic (platinum, paraffin) received a decided positive charge from organic acids, and a decided negative one from basic dyes. In this class the cases investigated are very numerous and the results quite unambiguous. Other basic organic substances (amidol, metol) and bases (barium hydroxide, soda-lime) also appear to charge negatively. Inorganic salts gave no well-defined results.

A substance, the surface of which reacts decidedly alkaline, such as glass, charges itself positively towards most substances. Only those substances which have a strong tendency to charge negatively, such as basic dyes, also produce a negative charge here.

A substance, the surface of which reacts sensibly acid, such as sulphur, charges itself negatively against the great majority of substances ; only substances which produce a strong positive charge like some organic acids (benzoic, salicylic) also produce a positive charge here.

If, however, the conditions of the experiment are chosen differently, we find that substances arrange themselves in similar classes, but that the sign of the charge is frequently reversed. Thus Rudge[2] made the following experiment. The fine dust of the various substances investigated was placed in a horizontal insulated cylinder of brass, which passed over into a cylinder of wire gauze. The latter was connected to a gold-leaf electroscope. A current of air from bellows drove the dust against the cylinder. It could be shown that the charge thus observed was upon the dust, the opposite charge being in the air. In this case the dust of sulphur and other non-metals (such as carbon, silicon, selenium, iodine) charged itself positively, as did also the organic acids ; while most metals, alkaloids, and other basic substances gave a negative charge.[3]

It is obviously necessary to analyse every frictional electrical process,

[1] Zeitschr. f. physik. Chemie, **39**, 225 (1902).

[2] Phil. Mag. (6), **25**, 481 (1913).

[3] Fine *Lichtenberg* figures could be obtained with the most various substances, when the cloud of dust was driven against a charged ebonite plate.

particularly with the object of deciding which electrical double layer is actually torn apart, how thick the adsorbed layer of water is under the experimental conditions, how strong the mechanical tangential force is, and what are the rubbing surfaces. It must be remembered that we have two solid phases—in the experiments of Rudge fine particles of dust probably rub upon coarser ones—both phases have their adsorption layers, consisting principally of water, in which a diffuse double layer lies. If the layer is thick enough, two double layers are present; one on the wall of the solid, which would show itself in the kataphoresis of the latter, and one at the surface towards the gas, as was assumed in the cases of kataphoresis of gas-bubbles and in ballo-electric processes. Upon close contact of the rubbing particles the adsorption layers are partly combined, during the rubbing they are again torn apart. Where this process of shearing will tear the double layer cannot be predicted and can only be determined by particular examination of the experimental conditions. Anyhow, it is not difficult to recognize that according to the circumstances the particles may remain behind positively or negatively charged.

The Union of Jets, Drops, and Bubbles under the Influence of Electrical Forces

Although this phenomenon has not the importance in connexion with the coagulation of colloidal solutions which was imagined in the first edition of this book, it none the less deserves to be treated of shortly. The process in question may show itself in various forms. If two soap-solution lamellæ are pressed against each other with a certain pressure, they unite after an interval of time; if one is given a small difference of potential towards the other, they unite much more quickly, at quite moderate values of the P.D. instantaneously.[1] Two jets of liquid, close to one another and issuing horizontally from a wall, do not usually unite at once when they touch, but generally rebound from each other; here also a small P.D. causes them to flow together.[2] In spite of the fact that the surface tension strives to unite the separated masses of liquid, the last layer of air separating them is difficult to press out. This is due to the fact that as the space in which the layer of air has to move gets smaller and smaller, the viscosity of the latter hinders its rapid motion more and more; this thin layer of air therefore behaves as if it were in a space closed on all sides, that is, like an elastic cushion, as in the phenomenon of the spheroidal state (cf. p. 101). The correctness of this view is proved by the fact that the two jets which meet and rebound prove to be electrically insulated from one another, and that optical-interference methods allow of the detection of the intervening air-layer in the case of two soap-bubbles touching one another. A slight mechanical pressure hastens the outflow of air, and potential differences do so for the same reason. Kaiser pressed a soap-bubble against a soap-water lamella, and determined the size of the surface of contact and the thickness of the intervening air-layer. Upon calculating the attraction due to a known P.D. he found the value to be 50 dynes, which value had been also found sufficient when applied mechanically. The E.M.F. of a Daniell cell reduces the time for union of bubble and lamella to about one-third. In the union of two jets, P.D.'s of $\frac{1}{2}$ to $\frac{1}{3}$ volt produced sensible effects.

To this group of phenomena belongs the influence of electricity upon the

[1] *Boys*, Phil. Mag. (5), **25**, 409 (1890); *E. Kaiser*, Wied. Ann. **53**, 667 (1894).
[2] *Rayleigh*, Proc. Roy. Soc. London, **28**, 406 (1879); **34**, 130 (1882).

breaking-up of jets into drops, also investigated by Rayleigh,[1] and the rolling of drops upon liquid surfaces, and other matters.

It is quite obvious that chance contaminations, specks of dust, etc., must strongly influence these phenomena. Not only are electrical differences introduced, at each such raised point (assuming the presence of a speck of dust) the distance apart of the masses of liquid is reduced, point effects arise, so that electrical forces are particularly active there. Rayleigh was able to show that the frequently observed chance union of two jets—which would otherwise have required electrical force to effect it—was determined particularly by dust suspended in the liquid.

It might appear curious that electricity exerts an influence upon the separation into drops of a single jet of liquid. As is particularly easy to see in the case of a jet rising vertically, weak electric forces act in the sense of preventing the jet from falling into drops. This does not, however, depend upon the point at which it breaks into drops being removed to another position ; the true explanation is as follows. The spraying of the jet into drops is due to the fact that the drops into which the jet is converted by the surface tension are not of uniform size, and do not move equally fast ; hence they collide with one another and rebound. An electrified body does not influence the various drops exactly equally ; potential differences arise between the separate drops themselves according to their distance from the electrified body, their size, and so on ; these differences may lead to parts having an opposite charge coming opposite to one another, so that when they collide they do not rebound, but combine. With strong electrical charges these differences in the charge disappear and the jet again breaks up, this time more strongly than it did without electrical influence, since the mutual repulsion of like charges on the drops takes effect.

Since the surface-active substances also show capillary-electrical activity (see p. 280), it is not surprising that they influence the flowing together of drops and jets. Rayleigh [2] mentions experiments from which the conclusion may be drawn that fatty acids and milk favour in a striking manner the union of two masses of liquid. Experiments on solutions of the organic dyes so active in ballo-electricity are not at present available.

(*b*) The Electrocapillary Curve

The Electrocapillary Curve of Mercury in Capillary-inactive Aqueous Solutions

The electrocapillary phenomenon which was earliest investigated is the action of the electrical current upon the interfacial tension of mercury against aqueous solutions. It and related phenomena will be referred to below as *electrocapillary*.

As far back as the beginning of the nineteenth century [3] experiments were repeatedly described in which the form of a mercury drop in an aqueous solution, and therefore its interfacial tension against this solution, was altered under the influence of an electric current. But G. Lippmann [4]

[1] *loc. cit.* p. 285. Particularly also *E. F. Burton* and *W. B. Wiegand*, Phil. Mag. (6), **23**, 148 (1912).

[2] Proc. Roy. Soc. **34**, 130 (1882).

[3] See on this point *Graetz*, "Über die Bewegungserscheinungen an kapillaren Quecksilberelektroden." Diss., Breslau, 1879.

[4] Pogg. Ann. **149**, 547 (1873), Ann. de chim. et de phys. (5), **5**, 494 (1875) ; **12**, 265 (1877) ; Wied. Ann. **11**, 316 (1880).

was the first who succeeded in so arranging the experiments that a numerical connexion between interfacial tension and electrical polarization clearly appeared.

His experimental arrangement was the following (see Fig. 57). The interfacial tension of the mercury against the aqueous solution was measured with a mass of mercury contained in a tube R; the latter ended in a fine point K, which dipped into the aqueous solution contained in the beaker G. The relative value of the interfacial tension was determined by adjusting the mercury to a definite position in the capillary by increasing or decreasing its height in the tube R. At the bottom of the beaker G was a mercury mass of large surface. This was connected to the positive pole, and the mercury in the tube with the negative pole, of a source of electricity. The small electrode is, on account of its small size and the slow diffusion of the ions into the capillary tube, polarizable; the large electrode may be regarded as unpolarizable. It is not permissible to polarize the small electrode

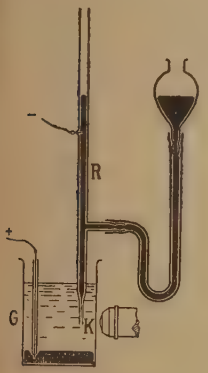


Fig. 57.

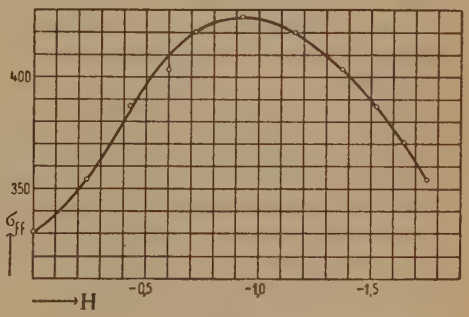


Fig. 58.—Electrocapillary Curve.

positively, as the meniscus oxidizes too strongly and prevents the measurement of the interfacial tension.

Other methods have also been employed to determine the interfacial tension in such experiments; for instance, the method of surface curvature,[1] drop-weight,[2] and large flat drops.[3]

If the values of σ_H which are found when negative potentials H (in volts) are applied to the small electrode, and may be ascribed to conditions of equilibrium, are plotted against the potentials, the electrocapillary curve represented in Fig. 58 is obtained. It is distinguished by a well-marked maximum. In order to interpret its course, Lippmann and Helmholtz [4] regard the electrical double layer on the surface of the small electrode as a condenser; they therefore assume that the electricity supplied by the current serves only to charge this condenser. The charge originally present upon the mercury surface reduces its surface tension, since similarly charged elements of the surface repel one another and this repulsion opposes the tendency of the interfacial tension to reduce the size of the surface. If the

[1] *König*, Wied. Ann. **16**, 1 (1882).
[2] *Kučera*, Ann. d. Physik (4), **11**, 529, 698 (1903).
[3] *Gouy*, Ann. d. Physique (9), **6**, 5 (1916).
[4] Gesamm. Abh. I, p. 925; also *König, loc. cit.* under [1].

original charge is diminished by addition of an opposite charge, the surface tension is increased. The original charge must be positive, since the addition of negative electricity increases the interfacial tension. σ_{fl} attains a maximum as soon as the charge reaches zero value. If by stronger polarization a negative charge is given to the mercury, this again causes for a like reason a diminution of σ_{fl}.

The interfacial tension is thus regarded one-sidedly as a function of the polarization, without any influence of dissolved substances upon the interfacial tension being taken into account; adsorption is neglected. E. Warburg [1] has developed another theory of this phenomenon. He does not assume any charging effect of the current, but only takes into account the changes in concentration produced by it at the electrodes. But he regards the adsorption as of essential importance, in particular that of the mercury salt, the positive adsorption of which causes the original σ_{fl} of the mercury to be so small. The electrical current discharges the ions of the adsorbed salt, lowers its concentration, and thus produces the increase in σ_{fl} with increasing negative polarization. In order to explain the descending branch of the curve which follows the maximum, E. Warburg and G. Meyer [2] assume that σ_{fl} is again lowered by deposition of H_2 and formation of amalgam. G. Meyer [3] points out that alkali metals dissolved in mercury lower its surface tension against alkali solutions even at very small concentrations.

Nernst [4] has discussed the course of the electrocapillary curve of mercury from the standpoint of his theory of the potential of metals in solutions. Since a mercury electrode has a strong positive charge when the concentration of mercurous ions in the solution is considerable, and this charge decreases and finally becomes negative when the mercurous ion concentration of the solution decreases sufficiently, σ_{fl} should also pass through a maximum as the mercurous ion concentration falls off, and it should then decrease, if the interfacial tension is, as expected, a function of the potential. σ_{fl} actually showed the behaviour expected; it went through a maximum and then decreased if, starting from a solution of mercurous nitrate, the mercurous ion concentration was greatly decreased either by addition of Cl′-ions or by addition of KCN.

But, as F. Krüger [5] points out, the Nernst double layer behaves on the passage of a current in part as a condenser, for since the surface density of the electricity upon the surface of the mercury changes with the mercurous ion concentration, mercurous ions must enter or leave the surface; that is to say, part of the current serves to alter the charge upon the surface, as in the case of a condenser. The Lippmann-Helmholtz theory holds, only that instead of a charge, mercurous ions are added or taken away.

Now, it is certainly incorrect simply to neglect the adsorption of capillary-active electrolytes and non-electrolytes, as is done in these theories. As we know from other boundary surfaces, the alteration in interfacial tension produced by active substances is as great or greater than that which is here ascribed only to the condenser action or the exchange of mercurous ions. Hence the ordinary adsorption of all substances present must always

[1] Wied. Ann. **38,** 321 (1889); **41,** 1 (1890).
[2] Wied. Ann. **45,** 508 (1892); **53,** 845 (1894); **56,** 680 (1896); **67,** 433 (1899).
[3] Zeitschr. f. physik Chemie, **70,** 315 (1910); regarding the surface tension of amalgams, see further *F. Schmidt* [Ann. d. Physik (4), **39,** 1108 (1912)].
[4] Beilage z. Wied. Ann. **58** (1896); Zeitschr. für Elektrochemie, **4,** 29 (1897).
[5] Nachr. d. Kgl. Ges. Wiss. Göttingen, 1904.

be introduced, as was done by Gouy [1] and simultaneously in the first edition of this book.

There are, however, limiting cases, in which the direct alteration of σ_{fl} by dissolved substances may be neglected as compared with the electrical alteration, namely, the capillary-inactive solutions. These are the dilute solutions of many inorganic electrolytes, especially the carbonates, phosphates, sulphates, and nitrates of the alkali metals; mercury in a KNO_3 solution may be taken as a good example of such a limiting case. To it we may apply without hesitation the thermodynamic argument, which according to Lippmann and Helmholtz gives the quantitative relation between σ_{fl} and the charge e of the surface.

The surface of the small electrode ω is increased by $d\omega$, and the work $-\sigma_{fl}d\omega$ is done. The charge e of the electrode is to remain unchanged, but the potential difference ε of the double layer, the phase-boundary force, assumes the value $\varepsilon - \frac{\delta\varepsilon}{\delta\omega}d\omega$; the potential falls when the surface is increased. If now the charge be increased by de, the work $\left(\varepsilon - \frac{\delta\varepsilon}{\delta\omega}d\omega\right)de$ is done; $\omega + d\omega$ is not hereby changed, but σ_{fl} becomes $\sigma_{fl} + \frac{\delta\sigma_{fl}}{\delta e}de$. The surface is now brought back to its original size ω, and the work $\left(\sigma_{fl} + \frac{\delta\sigma_{fl}}{\delta e}de\right)d\omega$ is gained. Finally, the surface, which has again assumed the potential ε, is relieved of the charge de and work $+\varepsilon de$ gained. Since the sum of the work of this isothermal process must be zero, we get

$$\frac{\delta\sigma_{fl}}{\delta\varepsilon} = -\frac{\delta e}{\delta\omega} = -\mathfrak{e} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\mathfrak{e}$ is the electrical charge upon unit of surface.

The maximum of the σ_{fl}, ε curve is reached when $\frac{\delta\sigma_{fl}}{\delta\varepsilon} = -\mathfrak{e} = 0$ and hence when ε is also zero.

In this argument only the charge of one side of the double layer is taken into account, namely that in the mercury. But we must suppose that the other side lying in the electrolyte acts in a similar sense.[2] For it was assumed for the double layer present at the boundary surface (cf. p. 241) that a firmly adherent film of water is attached directly to the second phase, in which film the second stratum of the diffuse double layer is in part contained. The properties of the boundary surface and hence of the interfacial tension are thus necessarily compounded of those of the surface of the mercury and of the adhering film of water. If this is taken into consideration, the repellent action is twice as great and we must employ the equation

$$\frac{\delta\sigma_{fl}}{\delta\varepsilon} = -2\mathfrak{e} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we ascribe with Lippman a constant capacity q to the condenser, $\mathfrak{e} = q\varepsilon$ and equation (2) may be integrated

$$\sigma_{max} - \sigma_{fl} = q\varepsilon^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

[1] In particular Ann. de chim. et de phys. (7), **29**, 145 (1903); (8), **8**, 291 (1906); (8), **9**, 75 (1906).

[2] *Krüger* and *Krumreich*, Zeitschr. für Elektrochemie, **19**, 620 (1913).

The equation to a parabola is thus obtained, which lies symmetrically to the axis passing through the maximum interfacial tension σ_{max}.

That in limiting cases equation (3) is largely fulfilled was shown by Krüger and Krumreich.[1] They determined the curve for mercury in a 1N-KNO_3 solution, in which therefore by the action of atmospheric oxygen some $HgNO_3$ or products of its hydrolysis had been formed. KNO_3 is but little active at mercury surfaces, and $HgNO_3$ also appears to be the least active of the mercury salts. It is also but little complex. Fig. 59 shows how well the observed curve (firm line) agrees with the calculated parabola (dotted). In it the ordinates are the applied pressures of the mercury column $h - h_0$, which are proportional to the σ_g values. The abscissæ are the polarizing voltages H applied from without. From these measurements we deduce a polarization capacity of 13·5 microfarads. Krüger[2] had found earlier from the electrical self-oscillation of polarized mercury cells a value in good agreement with this, viz. 13 microfarads.

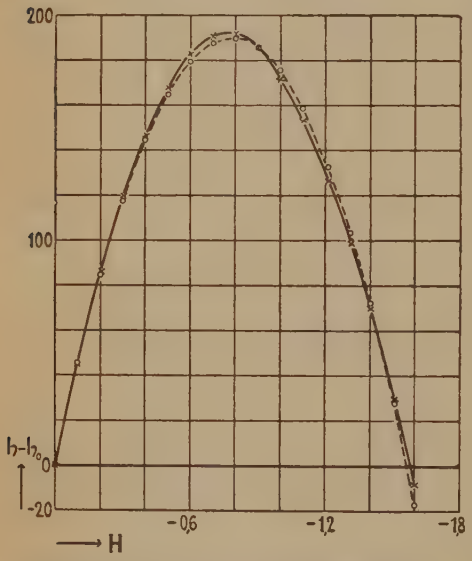


Fig. 59.—Theoretical and Experimental Electrocapillary Curve in Aqueous KNO_3 Solution.

We may therefore assume, almost with certainty, that in capillary-inactive solutions of electrolytes matters are very much as required by the Lippmann-Helmholtz theory. The double layer behaves like a condenser, at the maximum of the electrocapillary curve we have zero charge, the mercury has a positive charge on the ascending limb of the curve, and a negative one on the descending limb. In the various capillary-inactive solutions of electrolytes the σ_g, ε curves (or σ_g, H curves, as the case may be) only differ in so far as they have different initial points, since the original charge of the mercury is different in the different solutions; they may therefore be made to coincide by parallel displacement. The same is true when the concentration of the electrolyte alone is changed. The value of σ_{max} amounts, according to Gouy, to 426·7 dyne/cm. at 18°.[3]

Among the consequences of these relationships of the σ_g, ε curve, one confirmed by Pellat[4] may be mentioned. At the maximum, where the charge is zero, an increase or decrease of the boundary surface of the mercury causes no electric current to pass between this surface and another electrode, but a current does pass if the variable mercury surface according to its voltage is on the positive or negative branch, since the boundary surface

[1] Zeitschr. für Elektrochem. **19**, 617 (1913).
[2] Ann. d. Physik (4), **21**, 701 (1906).
[3] Ann. de Phys. (9), **6**, 25 (1916).
[4] Compt. rend. **104**, 1099 (1887).

must be charged up on increasing, and must give up charge on decreasing. The current in the two branches of the curve has opposite signs.

The change of the σ_{ff}, ε curve with temperature is slight.[1]

The Electrocapillary Curve of Mercury in Capillary-active Aqueous Solutions

If we have capillary-active solutions, two possibilities must be dis-distinguished :

1. Capillary-active solutions of non-electrolytes such as alcohols, amines, phenols, etc. Since their pure solutions are too bad conductors, Gouy [2] in his experiments always added a capillary-inactive electrolyte, generally Na_2SO_4.

2. Solutions of capillary-active electrolytes.

One might expect to succeed best in differentiating the influence of the adsorption of capillary-active substances, when the charge of the mercury surface is zero, when therefore we are at the maximum of the σ_{ff}, ε curve. We do actually find, when we use electrolytes to trace the dependence of σ_{max} on the nature and concentration of capillary-active substances, a complete repetition of all phenomena met with earlier at the interfaces liquid—gas and solid—liquid. This must necessarily be expected, as has just been remarked, if the film of water containing the surface-active substance adheres firmly to the mercury surface.

1. The lowering of σ_{max} in its dependence on the concentration of the dissolved substance may be calculated from the Szyszkowsky formula (see p. 63) :

$$\Delta = \frac{\sigma_{max_M} - \sigma_{max_L}}{\sigma_{max_M}} = \mathfrak{b} \log\left(\frac{c}{\mathfrak{c}} + 1\right).$$

As an example we may take the depression produced by pyridine ; the solution was normal with respect to Na_2SO_4.

Table 90

Depression of σ_{max} of Mercury with respect to an Aqueous Solution by Pyridine

$\mathfrak{b} = 0{\cdot}02416$; $\mathfrak{c} = 0{\cdot}02122$

c of Pyridine (Mol. per L.).	σ_{max} (obs.).	σ_{max} (calc.).
$\frac{1}{\infty}$	426·7	426·7
0·010	422	423
0·100	409	409
0·333	397	398
1·000	387	387

[1] See *G. Lippmann*, Ann. de chim. et de phys. (5), **12**, 275 (1877) ; *Paschen*, Wied. Ann. **39**, 64 (1890) ; *Cantor*, Wied. Ann. **47**, 418 (1892) ; *Kandidow*, J. russ. phys. chem. Ges. **45**, 707 (1913), cited from Chem. Zentralbl. 1913, II, 1541.

[2] *loc. cit.* p. 289.

2. Traube's rule holds for rise in a homologous series. Since only a few substances were measured by Gouy in a considerable number of concentrations, their c values for the Szyszkowsky formula cannot be evaluated; on the other hand, many substances were measured at a definite equal concentration, and hence the q values (cf. p. 66) are compared in the following table.

TABLE 91

Traube's Rule for the Depression of σ_{max} of Mercury against Aqueous Na_2SO_4 Solution by Alcohols

Substance.	Concentration.	$\Delta = \sigma_{max}$ M $- \sigma_{max}$ L.	.
Methyl alcohol	1 mol.	0·006	—
Ethyl alcohol	,,	0·021	3·5
n-Propyl alcohol	,,	0·071	3·4
Tertiary butyl alcohol	0·1 mol.	0·017	—
Tertiary amyl alcohol	,,	0·051	3·0

3. Aromatic substances and those of high molecular weight depress σ_{max} more strongly than aliphatic, as in the adsorption upon charcoal and other adsorbents. Table 92 gives a series of examples of this behaviour.

TABLE 92

Modification of σ_{max} of Mercury against an Aqueous Na_2SO_4 Solution by Organic Substances

Substance.	c (in Mols).	$\Delta\sigma_{max}$ (in per cent.).
Ethyl alcohol	1	− 2·1
Tertiary butyl alcohol	0·1	− 5·1
Isobutylene glycol	0·1	− 1·0
Mannitol	0·1	− 0·6
Cane sugar	0·1	− 2·9
Phenol	0·1	− 8·6
Acetic acid	1	− 1·8
Sodium acetate	1	− 0·5
Oxalic acid	0·5	− 1·3
Potassium oxalate	0·5	+ 0·1
Citric acid	0·1	− 1·7
Benzoic acid	0·01	− 5·2
Salicylic acid	0·011	− 6·8
Tetraethylammonium hydroxide	0·1	− 0·1
Triethylamine	0·1	− 7·4
Triethylamine sulphate	0·1	− 0·6
Isoamylamine	0·1	− 6·5
Isoamylamine sulphate	0·1	− 0·8
Aniline	0·01	− 3·9
Aniline sulphate	0·01	− 0·3
Pyridine	0·01	− 4·6
Pyridine sulphate	0·01	− 0·8
Amygdalin	0·1	− 9·4

4. The complete σ_{max}, c curve has a course such as was described on p. 54. A value of σ is reached at comparatively low concentrations which differs but little from that of the pure substance; thus, for example, σ_{max} in a concentrated aqueous solution of tertiary amyl alcohol or pyridine differs but little from σ_{max} in pure alcohol or pyridine respectively. In agreement with this is the further fact that when Gouy calculates the amount adsorbed a according to the Gibbs adsorption formula from the σ_{max}, c curves, a maximum, an adsorption saturation, is reached, and a decline in the amount adsorbed takes place at still higher concentrations; we have the course described on p. 181, Fig. 35.

5. With rise of temperature the depressent action of active substances declines, as is true also for their action at other interfaces.

The capillary-active substance does not merely lower σ_{max}, but also displaces it. The electrocapillary curve 2 in Fig. 60, in presence of amyl alcohol, does not exhibit a maximum at the same point as the curve 1 for the pure solution.

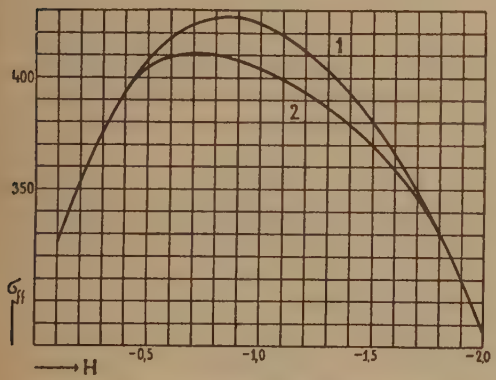


Fig. 60.—Displacement of the Electrocapillary Curve by Amyl Alcohol.

In many cases (alcohols, aldehydes, etc.) the maximum is displaced towards the positive branch of the σ_g, ε curve; in others (phenols, organic halogen derivatives, etc.) towards the negative. It will not therefore do to explain this by the influence which the alteration of the dielectric constant exerts upon a plate condenser of surface ω and distance of plates δ, according to the equation

$$e = \frac{\varepsilon D}{4\pi\omega\delta},$$

for since the dielectric constant of the organic substances in question is throughout decidedly smaller than that of water, this equation would only lead us to expect a change in the sense of a diminution in the charge, and not a displacement towards either positive or negative branch.

One must rather suppose that the potential curve of the phase-boundary force ε, in so far as it extends into the liquid according to the theory of the diffuse double layer, is decisively altered in its course by the organic substance present. Now σ_g by no means depends solely upon the numerical value of the phase-boundary force ε, concerning which we will first assume that the organic substance does not alter it, not even through an alteration in the dielectric constant—but it necessarily also depends upon the course of the potential curve in the layer of the aqueous solution adhering to the mercury. If the same external E.M.F. is applied as in the absence of the organic substance, this E.M.F. will not necessarily balance the effect of the organic substance on the course of the potential curve. Hence the same value of σ_g is not reached as in the absence of the sub-

stance in question. The maximum is therefore also displaced. Since it may be displaced either towards the positive or negative branch of the curve, the course of the potential curve must be susceptible to an influence from the organic substance in polarly opposed ways.

It is surprising that organic non-electrolytes have such an action. It is necessary, in order to explain it, to assume with Gouy [1] that the capillary-active dielectric non-electrolyte is polarized either in a positive or a negative sense by the forces of adsorption; it is doubtless a question of the similar orientation of the molecules at the boundary surface, which turn one group towards the mercury side, another towards the water; how successfully Langmuir and Harkins have applied this view to other phenomena will be discussed later (p. 315). In any case, this is a new action, which was not contained in electrocapillary theory as hitherto developed; it may be designated as *electrotonic*. A connexion with the double refraction exhibited by organic substances in an electric field, which connexion might seem plausible, does not appear to exist. For in respect of electrical double refraction benzaldehyde and paraldehyde are, for example, decided opposites; benzaldehyde is strongly positive, paraldehyde strongly negative in its double refraction.[2] The maximum of the electrocapillary curve is however, according to Gouy,[3] displaced towards the positive branch with both substances.

If we consider the influence of non-electrolytes on the two branches of the σ_{ff}, ε curve, Fig. 60 teaches us that at a certain distance from the maximum both the positive and negative branches of curve 2 coincide with those of curve 1. This is easily understood when we consider that on these branches the mercury is more strongly charged and the double layer correspondingly (cf. p. 254) much less thick. In those regions there are opposite the mercury surface only mercurous ions or the anions which preponderate in the solution; between the two strata of the layer there are no molecules of the organic non-electrolyte, which could change the course of the potential.

Here again (see p. 277) we must remember that the influence of foreign substances upon the electrocapillary curve can very well make itself felt in concentrations in which ordinary electrokinetic phenomena practically disappear; the double layer is still thick enough to allow of the influence upon the electrocapillary curve, but no longer thick enough to make itself felt by electrokinesis. This is quite apart from the fact that in electrokinesis, on account of the greater conductivity of more concentrated solutions, only small potential differences are measured, while in the electrocapillary curve these influences of conductivity do not come into account.

Before we deal with electrolytes with active ions, we may review the behaviour of electrolytes in general, also of the capillary-inactive ones. As in the cases of the surface tension water—air and of adsorption by charcoal and other adsorbents we encounter in the influence of electrolytes upon σ_{max} the lyotropic series (cf. p. 57); for anions the order

$$CO_3,\ PO_4,\ SO_4 > Cl > NO_3 > CNS,\ I,$$

for kations

$$Li > Na > K.$$

[1] Ann. de Physique (9), **7**, 125 (1917).

[2] See *A. Lippmann*, "Elektrische Doppelbrechung in Flüssigkeiten." Diss., Leipzig, 1912, pp. 167–8.

[3] Ann. de chim. et de phys. (8), **8**, 325 (1906).

TABLE 93

Change of σ_{max} of Mercury in Aqueous Solutions of Inorganic Electrolytes in 1-molar Solution [1]

Ion.	H (per cent.).	Li (per cent.).	Na (per cent.).	K (per cent.).	NH_4 (per cent.).
I	− 6·2	− 6·2	− 6·3	− 6·0	—
CNS . . .	− 4·7	—	− 4·2	− 4·4	− 4·7
Br . . .	− 2·5	− 2·2	− 2·1	− 2·1	− 3·3
NO_3 . . .	− 1·5	− 1·2	− 1·1	− 1·2	—
Cl	− 0·9	− 0·6	− 0·6	− 0·6	—
SO_4 . . .	− 0·3	+ 0·1	+ 0·2	+ 0·2	+ 0·2
HPO_4 . .	− 0·2	—	—	+ 0·3	—
CO_3 . . .	—	—	+ 0·2	+ 0·3	—

Fig. 61 shows how for the capillary-inactive phosphates, carbonates, sulphates, the rise in σ_{max} with the concentration, which is given in mol

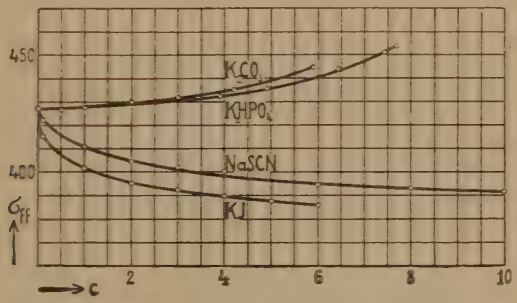


FIG. 61.—Change in the Maximum of the Electrocapillary Curve by Salts.

per litre, takes place practically linearly in dilute solution, as is also true in the case of the surface tension of water for many inactive electrolytes (cf. p. 56). The well-known and much greater action of the acids and alkalis, compared with their salts (cf. p. 60), is to be seen from Tables 92 and 93.

In the case of electrolytes with active ions similar relations hold as for active non-electrolytes. Only it is not necessary, in order to explain the displacement of the maximum, to have recourse to electrotonic influence; it is immediately evident that the course of the potential curve at the boundary surface will be changed and the maximum displaced on account of the distribution of the ions of the active electrolyte. For the capillary-active ions the direction in which the displacement will take place may be predicted. If the anion is active, then upon the positive, rising branch of the electro-capillary curve the side of the diffuse double layer which falls in the water will be decidedly richer in these anions. The interfacial tension, and therefore the aforementioned branch of the curve, will be strongly depressed, and also the region of the maximum, and only upon the negative, falling branch, where finally at considerable charges the capillary-inactive kations must preponderate in the water-layer, the depression of

[1] From measurements by *Gouy, loc. cit.* p. 289.

σ_{ff} by the anions disappears, and the curve then coincides with that found in the solution of capillary-inactive salts. Fig. 62A shows, along with the regularly electrocapillary curve 1 for a 1-molar Na_2SO_4 solution, the curve 2, in which the solution contained, in addition to the latter salt, also NaI, which in a concentration of 0·01 molar had an appreciable capillary action. The case of a capillary-active kation is symmetrically the converse. The negative branch is strongly depressed, and likewise the maximum; the

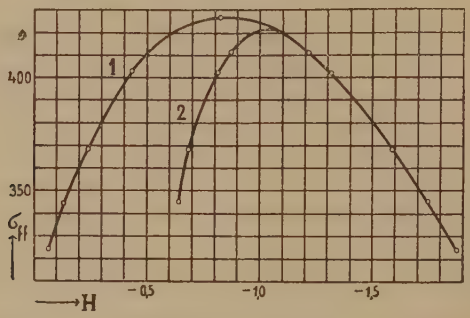


FIG. 62A.—Displacement of Electrocapillary Curve by Sodium Iodide.

rising positive branch remains unaltered. Accordingly we have the converse picture, Fig. 62B; curve 1 is a regular electrocapillary curve with 0·5-molar H_2SO_4 solution; for curve 2 the solution contained, besides the acid in the same concentration, caffeine in a concentration of 0·01 molar. In agreement with this view acid dyes displace the maximum towards the negative branch, basic towards the positive.[1]

The sense of the charge, which the maximum of the electrocapillary

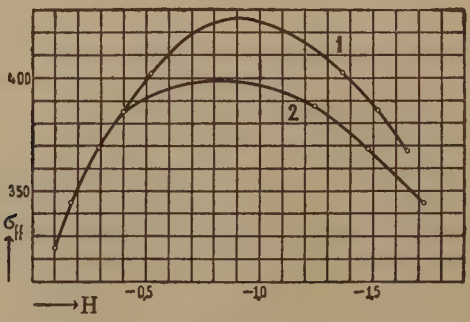


FIG. 62B.—Displacement of the Electrocapillary Curve by Caffeine.

curve in solutions of capillary-active ions shows, may also be recognized as follows. At the maximum of the electrocapillary curve no change of σ_{ff}, and hence no change in the concentration of the solution, may take place upon a change in the potential difference, due for instance to an enlargement of the mercury surface. If for example we have capillary-active anions, the Hg must carry a negative charge at the maximum point in order to balance the tendency of the anion to adsorption and the change in concentration

[1] *Freundlich* and Frl. *Wreschner*, Kolloidzeitschr. **28**, 250 (1921).

of the solution which it would produce. With capillary-active kations the mercury must have a corresponding positive charge at the maximum point.

In one point there is a contrast between electrolytes with capillary-active ions, and active non-electrolytes. With active ions there is no reason why the interfacial tension on the branch of the curve with opposite charge should not be sensibly depressed even at high charges. The side of the double layer in the water may even then be rich in oppositely charged active ions. We see, for example, from Fig. 62A how the positive branch is strongly depressed from the commencement, that is, even at considerable charges. With active non-electrolytes this was not, it will be remembered, the case (see p. 294). At considerable charges the surface layer was comparatively poorer in non-electrolyte, since the inactive ion of opposite charge is more plentiful there and the thickness of the double layer less. A peculiarity which follows from this behaviour is, that the breadth of the σ_{ff}, ε curve, that is, the difference of E.M.F.'s ($H_2 - H_1$) for a given σ_{ff}, is smaller for an active ion than for the unchanged electrocapillary curve.

In general, the depressent and displacing influence exerted by an active ion upon an electrocapillary curve will be more pronounced, the more adsorbable it is. This does not however exclude the possible existence of ions which also exert an electrotonic effect. With these the change in the electrocapillary curve would not be immediately deducible from the adsorbability of the ions.

The dependence upon capillary-active substances, as found in the electrocapillary curve, is in a notable manner intermediate between the dependence of the electrokinetic potential difference upon these substances and the dependence shown by potential differences measured transversely in galvanic cells. In the electrokinetic processes it is simply a question of the side of the double layer which falls in the water phase and hence of the potential difference ζ. The capillary properties of the electrolyte preponderate. The ion which determines the phase-boundary force ε (metallic ion of the electrode metal, $H^{\cdot}$ or OH' ions in the case of glass, etc.) becomes less important. In the case of galvanic cells, on the other hand, we only encounter this influence of the ion determining the phase-boundary force; that of the capillary-active substance does not produce any effect (cf. p. 251). But in the electrocapillary curve the interfacial tension is affected by both influences. The mercurous ion is important, since ε depends upon it and this alters the interfacial tension. But the capillary-active substances are not without influence; concentrated in the aqueous boundary layer, they depress σ_{ff} and are further electrically active, since they decide the course of the potential curve in the aqueous phase and the interfacial tension depends upon this also.

The Determination of Single Potential Differences by Means of the Electrocapillary Curve and Dropping Electrodes

Following Helmholtz,[1] W. Ostwald [2] pointed out that with the aid of the electrocapillary curve single potential differences at an electrode, and hence the absolute zero of potential, could be determined, while the measurement of galvanic cells always gives the sum of at least two potential differences. If in the arrangement shown in Fig. 57 the potential difference at the small electrode at the maximum point of the σ_{ff}, ε curve is

[1] See *A. König*, Wied. Ann. **16**, 35 (1882).
[2] Zeitschr. f. physik. Chemie, **1**, 583 (1887).

zero, then the E.M.F. applied from without must be equal to the only remaining potential difference, viz. that between the large mercury electrode and the solution. This single potential difference is therefore measured by determining the E.M.F. necessary to charge the Hg up to the σ_{max} point. From the above considerations it follows that this can only be true for capillary-inactive solutions, in which actually at the maximum of σ_{ff} zero voltage exists at the mercury surface. Table 94 indeed shows that for the cell with capillary-inactive solutions

$$Hg \mid Hg_2SO_4 \parallel Hg_2Cl_2 \mid Hg$$

the difference of the single potential differences ε_1 and ε_2 agrees with the E.M.F. E of the cell as directly determined. The difference of the single potential differences is simply the horizontal distance of the maxima of the electrocapillary curves measured in the two electrolyte solutions.

TABLE 94

Single Potential Differences from Electrocapillary Curves and E.M.F. of Galvanic Cells [1]

Cell.	ϵ_1, Single Potential Difference of first Electrode (in volts).	ϵ_2, Single Potential Difference of second Electrode (in volts).	$E = \epsilon_1 - \epsilon_2$.	E (obs.).
$Hg\|Hg_2SO_4\|\|Hg_2Cl_2\|Hg$	− 0·926	− 0·560	− 0·366	− 0·369
$Hg\|KCl\|\|KI\|Hg$ . . .	− 0·560	− 0·437	− 0·123	− 0·348(!)
$Hg\|KCl\|\|KCNS\|Hg$ . .	− 0·560	− 0·534	− 0·026	− 0·172(!)
$Hg\|KCl\|Na_2S\|Hg$ . .	− 0·560	+ 0·030	− 0·590	− 1·006(!)

This argument does not hold for capillary-active solutions. Here the charge at the maximum of the σ_{ff}, ε curve is not zero, since the maximum is displaced according to the nature of the active substance towards the positive or negative branch. The E.M.F. required to charge up to σ_{max} does not therefore give the single potential difference. Table 94 shows that in cells with active ions large deviations actually occur.

It appears however from what has been said that an active ion does not exert its disturbing influence upon the whole course of the σ_{ff}, ε curve; with an active anion, for example, the negative descending branch remains uninfluenced. If therefore we have electrocapillary curves of mercury against two solutions with different active anions, the negative branches lie as they would in inactive solutions. The horizontal distance between the two curves, as it is determined by the different mercurous ion concentration of the solution, and as it should obtain over the whole course of the curve in inactive solutions according to the Lippmann-Helmholtz-Nernst theory strictly applied, is therefore only regular between the negative branches. The E.M.F. of the chain should therefore be equal to this distance, even when the distance between the maxima, on account of the influence of the active ion, does not agree with this E.M.F. Table 95 shows from experiments by S. W. J. Smith [2] that this is quite correct.

[1] From measurements by *Rothmund*, Zeitschr. f. physik. Chemie, **15**, 1 (1894).
[2] Zeitsch. f. physik. Chemie, **32**, 433 (1900).

TABLE 95

Horizontal Distance between the Descending Branches of Electrocapillary Curves in Solutions with Active Anions and E.M.F.'s of Galvanic Cells

Cell.	Horizontal Distance of the Descending Branches of Electrocapillary Curves in the two Solutions (in volt).	E (obs.).
Hg | 0·5 norm. KCl Sol. || 0·5 norm. KI Sol. | Hg	— 0·399	— 0·394
Hg | 1·0 „ KCl „ || 1·0 „ KCNS „ | Hg	— 0·169	— 0·167
Hg | 1·0 „ KCl „ || 1·0 „ Na_2S „ | Hg	— 0·939	— 0·959

Before it was known upon what the influence of capillary-active substances upon the σ_{ff}, ε curve depended, a search was made for other electrocapillary arrangements for the measurement of single potential differences free from these disturbances. Helmholtz [1] already arrived at the view that a *dropping electrode*, in which Hg enters a solution in a fine jet and there breaks up into drops, has a potential very close to zero ; he assumed that charging up takes place slowly, and that therefore the distribution of the small charge originally present over the large freshly generated mercury surface produces the smallness of its charge. If a dropping electrode has zero charge, a similar stationary Hg electrode in the same solution should exhibit towards the dropping electrode the same potential difference as is necessary to polarize Hg in the same solution up to the σ_{max} point. This expectation was fulfilled in the case of capillary-inactive solutions, as the following table, taken from experiments by Paschen,[2] shows.

TABLE 96

Comparison of Single Potentials from Electrocapillary Curve and from Dropping Electrode

Solution.	E.M.F. required to charge up to σ_{max} (in volt).	Potential Difference between stationary and dropping Electrode.
Hg in 1 mol. HCl Solution . . .	— 0·560	— 0·557 to — 0·561
Hg in 0·1 „ NaCl „ . . .	— 0·560	— 0·557
Hg in 0·1 „ KBr „ . . .	— 0·494	— 0·493

The assumptions upon which Helmholtz based his work were only partially correct. First of all Paschen [3] found that it is not a question of reducing an existing charge by stretching the Hg surface, but rather of bringing the Hg jet for so short a time in contact with the solution that the

[1] *loc. cit.* p. 287.

[2] Wied. Ann. **43,** 585 (1891) ; *Paschen* has published the following papers on electrocapillary processes : Wied Ann. **39,** 43 (1890) ; **40,** 36 (1890) ; **41,** 42, 177, 186, 801, 899 (1890) ; **43,** 568 (1891).

[3] Wied. Ann. **41,** 801 (1890).

rapidly occurring process of charging cannot take place. The dropping electrode gives values in capillary-inactive solutions which agree with those deduced from the σ_{ff}, ε curve, if the jet breaks up into drops just at the point at which it meets the solution. This is easily understood from the theory of the dropping electrode as worked out by Nernst in accordance with his theory of the electrocapillary curve (cf. p. 288). The fresh surface of the mercury jet charges itself as it enters the solution, and hence removes mercurous ions from the solution or gives them off to it. The solution must therefore continue to become richer or poorer in mercurous ions at the point of entry of the jet, until no further tendency to exchange is present, until, therefore, the osmotic pressure and the solution pressure of the mercury opposed to it balance each other. Then, however, according to Nernst's theory, the phase-boundary force of the metal is

$$\varepsilon = \frac{RT}{nF} \log \frac{\Pi}{P} = 0$$

(where Π is the solution pressure of the metal, P the osmotic pressure of the mercurous ion in the solution).

This view is only correct when the solution at the point of entry of the jet does not continually receive fresh mercurous ions by diffusion or convection, which would cause depolarization of the mercury. Hence it is of advantage if the mercury jet itself only comes into contact with the solution over a very small space and time. It follows from this theory that mercury salt must be carried over from the dropping to the stationary electrode. Every fresh drop entering the solution charges itself, that is, mercurous ions are as a rule deposited upon it; and since a separation of anion and kation cannot occur, every drop is enveloped in a layer of anion. Below, where the mercury drops flow together, the salt carried down goes into solution; at the surface the concentration decreases, while it increases below. We should therefore have, on account of the action of the phase-boundary force, an "electrical adsorption" of the mercurous salt at the mercury surface; it would be distinguished from ordinary adsorption by the fact that the concentration of mercurous ions determines it, and that it is negative for very small concentrations of mercurous ions. The adsorption isothermal would thus have quite a different form. Palmaer [1] was able to show that a transference of mercury salt by the dropping electrode actually takes place.

But all this is true only for inactive solutions. In solutions with active ions we meet with the same deviations as in the σ_{ff}, ε curve, and further they are, as Paschen [2] was the first to show, numerically equal. The potential difference between a dropping electrode in the solution of an active ion and of an inactive ion is just as great as that between the σ_{max} values in the active and inactive solutions; naturally taking account of the regular displacement due to the different values of the original charge in the two solutions. In other words, the dropping electrode bears the same charge as mercury with the σ_{max} value in the same solution.

This may be interpreted as follows. The fresh mercury surface not only takes up (or gives off) mercurous ions, but also adsorbs the capillary-active ion. That this is true both for active anions and kations appears from the experiments of Patrick described on p. 91. At the point of entry

[1] Zeitsch. f. physik. Chemie, **25**, 265 (1898); **28**, 257 (1899); **39**, 664 (1901).

[2] *loc. cit.* p. 299; see also *S. W. J. Smith* and *Moss*, Phil. Mag. (6), **15**, 478 (1908).

of the jet there is a tendency towards a state in which the charge of the mercury balances the adsorption of the similarly charged ion. This is however the same assumption as was regarded on p. 296 as a condition for σ_{max} in active solutions.

This state of affairs is not changed by selecting, with Palmaer,[1] a solution of such composition that no current flows from the dropping to the stationary electrode. He then assumed that in such a *zero-solution* both electrodes have zero potential. This is however not correct, as S. W. J. Smith and Moss[2] show; different zero solutions have similar potential differences between themselves as have dropping electrodes. Only in a zero solution the dropping electrode has the same potential as the stationary one. For both therefore the condition holds as in the case of the agreement of the charge of the dropping electrode with that of the Hg at σ_{max}, viz. that charge and tendency to adsorption balance one another.

To summarize, we may say that in capillary-inactive solutions single potential differences may be determined both from the electrocapillary curve and by means of the dropping electrode; in capillary-active solutions both methods yield the same deviations. The absolute zero of potential, as derived from measurements in inactive solutions, lies at a value of about 0·57 volts against the decinormal calomel electrode, as already found by W. Ostwald.

Further Electrocapillary Phenomena at Mercury Surfaces

Möller[3] followed the dependence of the contact angle α, formed by a hydrogen bubble resting on a mercury meniscus (see Fig. 63), on the negative polarization of the mercury. The maximum value of α coincided with σ_{max}. This agrees with what one would expect. If we suppose that the contact angle corresponds to a state of equilibrium, then we have from p. 99

$$\sigma'_A - \sigma'_B = \sigma_{ff} \cos \alpha$$

where σ'_A and σ'_B are the equilibrium surface tensions of mercury and the aqueous solution against air, and σ_{ff} the interfacial tension of the mercury against the solution.

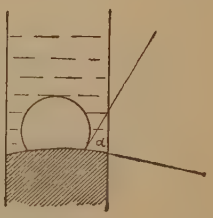


Fig. 63.

The surface tensions are practically unaltered by polarization; this appears from an investigation by Barnett.[4] He reviewed first of all the methods which could conceivably be applied or had previously been applied by other investigators, and showed that they are mostly unsuitable; on account of the great potential differences which are necessary, the direct mechanical action of the electricity, repulsion from the walls of the vessel, and so forth, cause alterations in the capillary rise, drop-weight, etc., so that no deduction can be drawn from these values as to the surface tension. Only the method of surface waves (cf. p. 15) is fairly free from objection; the surface of the liquid may be used as one plate of a condenser, and a layer of metal opposite to it as the other, and disturbances due to electrification of the walls of the vessel and like causes can be avoided. A direct electro-

[1] Zeitschr. f. physik. Chemie, **59**, 129 (1907).
[2] *loc. cit.* p. 300.
[3] Ann. d. Physik (4), **25**, 725 (1908).
[4] Physic. Rev. **6**, 257 (1898).

static influence is, however, in so far to be taken into account as similarly charged wave-crests repel one another and hence produce an apparent diminution of the surface tension; this influence may, however, be taken into account. The careful experiments of Barnett and Merritt [1] yielded the result that the surface tension is not altered by electrostatic charge within the limits of error of the experiment. Hence $\sigma'_A - \sigma'_B$ is as good as constant with increase of polarization. In order, however, that $\sigma_{ff} \cos \alpha$ may be constant, α must have a maximum value at the same time as σ_{ff}.

A further consequence of the form of the electrocapillary curve are the phenomena of motion, investigated especially by Christiansen,[2] which a mercury drop shows in an aqueous solution, when an electric current is passed through it. If the drop, as in a KNO_3 solution, is at first positively charged, it becomes egg-shaped at currents of about 10 milliamperes; at the point of entry of the current, where the drop is negatively charged, σ increases, the drop becomes pointed; at the exit of the current, where σ becomes smaller, the drop becomes flatter. Since the mercury on the surface of the drop is drawn from points of lesser to points of greater surface tension, it moves from the blunt end to the pointed one, as may be recognized from specks of dust upon the surface of the drop. On account of the law of action and reaction, the whole drop moves in the opposite direction, that is, towards the negative pole.

At greater currents of about 20 milliamperes a ring-shaped collar appears in the neighbourhood of the pointed end, which moves toward the middle of the drop as the current is increased, becoming more and more pronounced, until at a current of about 33 milliamps. a small drop is separated from the larger at its pointed end (see Fig. 64).

Fig. 64.

From a certain polarization onwards σ_{max} is reached at the pointed end of the drop, at higher polarizations the zone of σ_{max} wanders further along the drop, since all intermediate values of the potential distribute themselves in rings between the negative value at the pointed end and the positive at the blunt end; at the ring with potential zero σ has its maximum value, the surface is most strongly curved there; a collar results. The mercury moves from both ends towards the collar, and the counterflow can be strong enough to tear a drop off the end. If the current increases still further, σ_{max} on the collar will not become greater, but remain unchanged. Since σ at both ends, however, becomes still smaller, the gradient of σ is still steeper in both directions; the collar becomes still more pronounced, and a drop is finally separated off. This phenomenon is the converse of that described on p. 90; there the lowering of the σ of a drop of oil by means of a soap solution upon an equatorial line, here the increase of σ upon a corresponding line on a mercury drop up to the maximum of interfacial tension. If the mercury in another electrolyte solution (for instance, concentrated KCN) has a negative charge from the start, the phenomena are correspondingly reversed.

To this group of phenomena belong also those oft-described motions of a drop of mercury, which, for example, comes into one-sided contact with some potassium dichromate in an acid solution.[3] The drop first moves towards the potassium dichromate, then moves away again, and oscillates irregularly to and fro. This arises from the fact that the mercury, where it comes into contact with the dichromate, becomes oxidized; its tension is lowered thereby. As in the above-described experiments of Christiansen, the drop moves in such a way that the surface with lower tension is in front. The oxide formed dissolves in the acid, the parts of the surface attacked again become metallic, their tension becomes greater than other parts, and hence the direction of movement is reversed.

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[1] Physic. Rev. **10**, 65 (1900).

[2] Ann. d. Physik (4), **12**, 1072 (1903).

[3] See e.g. *Bernstein*, Pflüger's Archiv, **80**, 628 (1900); also *Quincke*, Wied. Ann. **35**, 580 (1888).

Electrocapillary Phenomena at other Boundary Surfaces

Various investigators [1] have measured electrocapillary curves for amalgams. As is well known, amalgams of metals less noble than mercury behave in electromotive respect like the pure metals when their content exceeds a certain amount of the latter. In capillary-inactive electrolyte solutions, and as long as the metal does not react with the solution, the E.M.F. necessary to polarize the amalgam to σ_{max} should be equal to the potential difference which the metal has against the solution in question. Amalgams do actually give in electrolyte solutions similar σ_{ff}, ε curves to those of Hg, and the expected relation is fulfilled for metals such as lead, bismuth, and copper to a considerable degree; to a much less degree for amalgams of metals which decompose acids.

Similar σ_{ff}, ε curves with a pronounced maximum have also been observed [2] for molten metals and alloys under aqueous solutions or molten salts, without anything new of theoretical importance appearing.

Möller [3] applied to other metallic electrodes the method described on p. 301 for the determination of the contact angle of a hydrogen bubble resting upon a metallic surface under the influence of polarization. For nickel, copper, and silver electrodes in decinormal H_2SO_4 he obtained a contact-angle polarization curve with a maximum. From the considerations on p. 302 this maximum should coincide with σ_{max} and hence correspond to the zero of potential. In all these cases the zero was indeed about $-0{\cdot}60$ volt, as compared with the decinormal calomel electrode, in satisfactory agreement with the value of $-0{\cdot}57$, which was determined from the electrocapillary curve of Hg (cf. p. 301).

A method for measuring single potentials can also be obtained by applying the experiments of Pellat described on p. 290 to other metals. A metallic wire is polarized in a solution and then stretched; a polarization is searched for at which as the result of stretching no current flows between the wire and another unpolarizable electrode contained in the solution. In inactive solutions the wire should then have zero charge. Krouchkoll [4] found in such experiments zero points of this kind and a reversal of sign upon stretching the wire, and the single potential differences measured in this way agreed not unsatisfactorily with the E.M.F. of cells measured under similar conditions of experiment.

As a converse of these experiments, in which an external E.M.F. causes the extension or contraction, as the case may be, of an electrode, Krouchkoll mentions an experiment of Gouy's. The latter dipped into the solution of an electrolyte a thin gold leaf insulated upon one side and rolled into a spiral, and polarized it against a second electrode. With a positive charge the leaf stretched, with a negative one it rolled itself together more closely, a sign that the gold was charged positively towards the solution. In all these experiments the phase-boundary force ε is altered transversely.

[1] *Rothmund, loc. cit.* p. 298; *G. Meyer,* Wied. Ann. **53,** 845 (1894); **56,** 680 (1895).

[2] *Paschen,* Wied. Ann. **40,** 36 (1890); *Luggin,* Zeitschr. f. physik. Chemie, **16,** 694 (1895); *Vining,* Ann. de chim. et de phys. (8), **9,** 272 (1905); *v. Hevesy* and *R. Lorenz,* Zeitschr. f. physik. Chemie, **74,** 443 (1910); *Luggin* and *v. Hevesy* and *Lorenz* have also investigated mercury and molten lead against molten salts.

[3] *loc. cit.* p. 301; further Ann. d. Physik (4), **27,** 665 (1908), and Zeitschr. f. physik. Chemie, **65,** 226 (1908).

[4] Ann. de chim. et de phys. (6), **17,** 129 (1889).

If, as up to the present, the one phase dealt with is a metal, matters are both theoretically and experimentally comparatively simple. Theoretically, because only one kind of ion, the kation—by preference the kation of the metal in question—passes from one phase into the other. At the boundary of two other liquids—say an aqueous solution and an organic liquid—one must, on the other hand, reckon with the transference and distribution of all kinds of ions present, as has already been discussed with reference to the relationship between phase-boundary force and electrokinetic potential difference (see p. 276). The conditions are simple experimentally, since it is easy to give the metallic phase a definite potential, which is a difficult matter in the case of liquids which do not conduct so well.

Hence few experiments have been made in this direction, from which, however, one can deduce that phenomena, similar to those at the interface mercury—aqueous solution, may be observed. Krouchkoll [1] set up a Lippmann capillary electrometer with ethyl ether saturated with uranyl nitrate as one phase, and an aqueous solution, also saturated, of the same substance as the other phase. He found a σ_{ff}, ε curve with a maximum, when the positive pole dipped into the aqueous, and the negative into the ethereal solution. A system carbon bisulphide—acidulated water behaved similarly. Further v. Lerch [2] described changes in form and motions of a benzene drop in aqueous electrolyte solutions, such as were described by Christiansen (cf. p. 302) for mercury drops. As already remarked on p. 276, previous investigations do not suffice to enable anything to be said with certainty about the phase-boundary forces at the interface of organic liquids and aqueous solutions. The distribution of the ions is without question of great importance, but it has not been possible hitherto to measure it satisfactorily. Nor is it clear how far the adsorption of the ions (and of the non-dissociated substances) must be taken into account. Further, it must be remembered that the various mobilities of the ions in the two phases give rise upon the passage of a current to changes of concentration at the boundary surface, which on their part must influence the interfacial tension.

One more fact is deserving of mention, namely, that it is not a matter of indifference from the electromotive point of view whether a surface of separation between two solutions of different concentration in the same solvent is continuous or as discontinuous as possible. Chanoz [3] investigated cells of the following type :—

A – B B – A

Reversible Electrode Zn in $ZnSO_4$ Solution	Aqueous Solution A	Aqueous Solution B	Aqueous Solution A	Reversible Electrode Zn in $ZnSO_4$ Solution

The arrangement was completely symmetrical excepting that, for example, the boundary A – B was entirely continuous, while B – A was as discontinuous as possible ; in the latter case solution A flowed in a stream into solution B. If B was pure water, A the aqueous solution of a pure electrolyte with only two ions, then no E.M.F. was observed ; but forces up to 100 millivolts and more appeared if solution A contained more than one electrolyte, the ions of which differed appreciably in migration velocity—for example, a solution of an acid and a salt. The direction of the E.M.F. was such as if

[1] *loc. cit.* p. 303. Similar experiments were performed by *Kandidow*, Zeitschr. f. physik. Chemie, **83**, 587 (1913).

[2] *loc. cit.* p. 87.

[3] Ann. de l'Université de Lyon, No. 18 (1906).

the quickly moving $H^{\cdot}$ ion charged the layer into which it entered more strongly positive at the discontinuous boundary than at the continuous one. Since quickly moving ions are also the ones to be strongly adsorbed, it is not impossible that adsorption causes the quick initial penetration of the active ion. Experiments with capillary-active dye ions are unfortunately not available. In any case one must reckon with an influence of this kind at dropping electrodes, and it is not impossible that certain peculiarities, which Kučera [1] observed on the σ_{ff}, ε curve of mercury, when he measured σ_{ff} by a more dynamic method, may be referred to this phenomenon.

(c) Influence of Adsorption upon Electrolytic Processes

The processes occurring at the electrodes during electrolysis are, as is well known, of great complexity. The influence of diffusion and of the velocity of chemical reaction, the formation of solid coatings upon the electrodes, and of alloys with the electrode metals, have already been followed in detail. Phenomena are now known in which one is inclined to assume the influence of adsorption.

Thus, Leblanc [2] describes cases in which the polarization at metallic electrodes (Cu, Ni and Fe electrodes) and at oxidation and reduction electrodes (ferric-ferrous, thallic-thallous, ceric-cerous) was increased by capillary-active substances such as strychnine and brucine or by colloidally dissolved substances such as gelatine.

In no case hitherto investigated has the rôle of the foreign substance been so carefully examined as to allow of a decision concerning the nature of its influence. That we are dealing with an adsorption is probable, since we have capillary-active substances. Further evidence in favour of this view is the observation of Leblanc [3] that in the electrolysis of ferro-ferric sulphate solution at gold electrodes the intensifying effect of the strychnine upon the polarization decreased considerably when the temperature was raised to 80°, and returned to its original power at ordinary temperature. This tells against Foerster's view [4] of the possible formation of coatings. The proof that the Traube rule holds for the foreign substances would however be very welcome.

If adsorption is involved, it might act in various ways. On the one hand it might be a question of the displacement discussed upon p. 145. The number of adsorbed molecules in the adsorption space of the electrodes should be constant. A strongly adsorbable substance will thus greatly reduce the concentration of the other kinds of molecules and so be able to cause polarization. This is a view especially upheld by Reichinstein.[5]

It is of course also possible that the electrode reaction which determines the chemical polarization takes place immediately at the electrode, and that the adsorbed substance forms a coating which hinders diffusion. We should thus be dealing with conditions similar to the oxidation of SO_2 on platinum (cf. p. 147) or of phenylthiourea on charcoal (cf. p. 230).

And finally, the adsorbed substance might also react directly with one of the substances taking part in the electrode reaction, and so lower its concentration.

[1] *loc. cit.* p. 287.
[2] Abh. d. deutsch. Bunsen-Ges. Nr. 3 (1910).
[3] Abh. d. deutsch. Bunsen-Ges., Nr. 3, p. 36 (1910).
[4] Elektrochemie Wässriger Lösungen, Leipzig, 1915, p. 736.
[5] *loc. cit.* p. 145.

Reichinstein [1] remarks that a similar inhibitory influence of foreign substances is also observed in other oxidation and reduction processes, as in the dissolution of many metals in oxidizing solutions (nickel in a chromic-sulphuric acid solution) in the rusting of iron and other cases.

Möller [2] would interpret also *over-voltage* entirely as a capillary chemical phenomenon. It consists in the fact that a gas in electrolysis does not separate at the potential calculated from the reversibility of the process, but at a much higher one. Möller assumes that in over-voltage we only have the work required to bring the gas in the boundary surface of the electrode to such a concentration that it can form a bubble. This work depends first of all upon the magnitude of the surface tension gas—electrolyte solution, for the greater this is, the greater the work required to generate the surface of the first bubble. If, however, the electrical forces alone have to bring about the accumulation of the gas in the surface layer, and the properties of the surface layer in no way favour this process, then the over-voltage will be particularly large. If on the other hand the gas, on becoming more concentrated, lowers the interfacial tension of the electrode against the solution, if therefore it is adsorbed, if further the electrode is well wetted by the electrolyte, so that the gas is indeed able to reach the boundary surface electrode—electrolyte solution, then the concentration of gas necessary for the formation of bubbles will be reached sooner; the over-voltage is therefore smaller, the smaller the interfacial tension electrode —electrolyte, and the more easily the electrode is wetted. Since the contact angle between gas-bubble and electrolyte solution is symbatic to the interfacial tension (cf. p. 302), contact angle and over-voltage must go parallel to one another.

Möller generated a hydrogen bubble upon a mercury electrode and determined the contact angle α (cf. p. 301). He then followed the alteration of this angle with the temperature, and further the alteration of the over-voltage with it. The two temperature curves were distinctly parallel and showed a maximum at 5°. Also in the case of the over-voltage of hydrogen at copper and silver electrodes this parallelism between the contact angle—temperature curve and the over-voltage—temperature curve reappeared. It is further in agreement with this theory that fatty impurities, which lessen the wetting, raise the over-voltage.

In detail, however, this mode of explanation meets with many difficulties. Thus the over-voltage ought to be greater on a smooth electrode than on a rough one, since for the latter the local overcoming of the surface forces is easier. But between smooth and rough lead electrodes no distinct difference in the over-voltage could be found, nor between liquid and frozen mercury.[3] Nor can the influence of the alloys and compounds of hydrogen with the electrode metals in the case of the over-voltage of hydrogen be simply interpreted upon the basis of Möller's theory. We may probably state that capillary chemical processes cannot be neglected in connexion with over-voltage, but that still greater importance is to be attached to

[1] *loc. cit.* p. 145; further also Zeitschr. f. Elektrochemie, **19**, 672, 914 (1913); **20**, 406 (1914); **21**, 359 (1915).

[2] *loc. cit.* p. 303.

[3] See *Coehn* and *E. Neumann*, Zeitschr. f. physik. Chemie, **39**, 353 (1902); Zeitschr. f. Elektrochemie, **8**, 591 (1902); particularly also *Foerster*, "Elektrochemie wässrigen Lösungen," Leipzig, 1915, p. 278.

the formation of alloys and hydrides and to the rate of dehydration of the ions.[1]

VI. The Properties of Interfacial Layers

Theoretical Considerations concerning the Thickness of the Interfacial Layer

It is particularly the question of the thickness of the interfacial layer which we encounter again and again. To answer it is not easy, and hence the Langmuir adsorption theory, which usually only assumes a single layer of molecules as adsorption layer, was previously (cf. p. 122) contrasted with that of Polanyi, who postulates a larger number of molecular layers, without a decision being made between the two theories. It is perhaps not correct to put the question in this general form, since probably from case to case the properties of the interfacial layer are too variable. What, however, has again and again led to the search for a general answer is the circumstance that a relation holds between the thickness of the surface-layer and the radius of the sphere of molecular action. Hence if we take up the standpoint that the forces with whose radius of action we are dealing are entirely chemical, that we are therefore dealing with the action of residual valencies, the question of the thickness of the surface-layer would at once amount to the other question: How far does the force of chemical attraction extend? If the latter question should allow of a more general answer, which, however, does not appear to me to be settled, this would also be so for the first question.

The connexion between thickness of the surface-layer and radius of molecular action becomes plain, when we consider that part of the surface-layer which lies in the liquid in the case of the transition from a liquid to a gas. Its thickness may be put equal to the radius of molecular action: for all layers of molecules lying at the boundary of the liquid which have properties different from the layers of molecules in the interior of the liquid will be reckoned as belonging to the surface-layer. All layers of molecules which have still so many layers of molecules over them in the direction towards the gas space as are necessary to exert the regular internal-pressure attraction, are under similar conditions of internal pressure. The necessary number of layers is given by the radius of molecular action. All layers of molecules which are at a distance from the boundary surface less than the radius of molecular action belong to the surface-layer. The same is true for the thickness of the surface-layer between a solid and a gas. The adsorption layer extends into the gas space, as we have repeatedly assumed, in particular on p. 122, and the limit of the adsorption space is also determined by the radius of the sphere of action. The total transition layer will therefore be of twice this thickness. When two liquids are in contact, or a liquid with a solid, it is at once evident that this is true, since we have in each phase a transition layer, as has just been assumed to exist in the transition of liquid to gas.

According to this we may deduce conversely the thickness of the surface-layer from the radius of molecular action. Now many theoretical considerations lead to the result that the latter is not sensibly greater than the diameter of a molecule. The transition layer at the boundary of two phases would thus only consist of two layers of molecules, one in each phase. This

[1] See also *Newbery*, Journ. Chem. Soc. **105**, 2419 (1914); **109**, 1051 (1916); **119**, 477 (1921). Dunnill, *ibid.*, **119**, 1081 (1921).

conclusion is reached *inter alia* by the following argument, due to Einstein.[1] In the equation of Eötvös (equation 3, p. 32) we may put instead of the molar free surface energy

$$\sigma(Mv)^{\frac{2}{3}}$$

the molar total surface energy (cf. p. 35)

$$U_\omega = \left(\sigma - T\frac{d\sigma}{dT}\right)(Mv)^{\frac{2}{3}}.$$

If we neglect in this the term τ of Ramsay and Shields (cf. p. 32), then we get the equation

$$U_\omega = \left(\sigma - T\frac{d\sigma}{dT}\right)(Mv)^{\frac{2}{3}} = k\theta_0. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Now the absolute boiling-point T_S is for non-associated liquids a constant fraction of the critical temperature θ_0. Further, Trouton's rule is approximately correct, that the molar internal latent heat of evaporation

$$U_i = M\lambda_S - RT_S$$

is proportional to the absolute boiling-point. (Here λ_S is the ordinary latent heat of evaporation at the boiling-point.) If we introduce into equation (1) instead of the critical temperature the corresponding function of U_i, we get

$$\frac{U_\omega}{U_i} = k' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

k' must be a function of the radius of molecular action. For if we imagine 1 gramme-molecule as a cube, then U_ω is equal to half the total change of energy which occurs when the cube is cut parallel to one of its faces and the two parts separated to a distance beyond the radius of molecular action. The radius therefore enters into this work. U_i is the change of energy when the whole cube is evaporated; it therefore increases with the length of the side of the cube.

Now it is surprising that such a relation as 2 should hold. For since U_ω is proportional to the quantity $(Mv)^{\frac{2}{3}}$, and U_i to the total molar volume Mv, then if the radius of molecular action were independent of the nature of the liquid, we should have

$$\frac{U_\omega}{U_i} = k''(Mv)^{-\frac{1}{3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In order to obtain equation (2) we must suppose that the radius of molecular action is proportional to $(Mv)^{\frac{2}{3}}$. Since $(Mv)^{\frac{2}{3}}$ is equal to the side of the cube representing the molar volume Mv, this simply means that the radius of molecular action is proportional to the distance of the molecules from one another.

Einstein emphasizes that this is best understood if the radius of the sphere of molecular action is equal to the diameter of a molecule, if therefore only adjacent molecules are under the influence of the molecular forces. He calculates $\frac{U_\omega}{U_i}$ by supposing the molecules to be arranged within a quadratic lattice, and considering an elementary cube, upon each of the

[1] Ann. d. Physik (4), **34**, 165 (1911). See also the very similar argument in *van der Waals-Kohnstamm*, Lehrb. d. Thermodynamik, Amsterdam-Leipzig, 1908, Vol. 1, p. 269, from which the conclusion is arrived at that the capillary layers of two liquids are to one another as the diameters of their molecules.

edges of which are three molecules, so that twenty-six molecules act upon the one situated at the centre of the cube, and thus obtains the equation

$$\frac{U_\omega}{U_i} = \frac{9}{26} N^{-\frac{1}{3}},$$

where N denotes the number of molecules in a gram molecular weight. We thus get

$$\frac{U_\omega}{U_i} = 4 \times 10^{-9}$$

(assuming $N = 60 \times 10^{22}$). By experiment we get from the values of U_i and U_ω for benzene, for instance, the value $5{\cdot}3 \times 10^{-9}$, in good agreement with the above. Now an agreement of this kind is preserved as regards its order of magnitude, if we imagine the attraction extended over two or three neighbouring layers of molecules. But it is not evident by what the limit is then still determined.

This argument would thus lead to ascribing to the surface-layer of one phase the thickness of one layer of molecules, that is, less than 1 $\mu\mu$.[1]

Langmuir comes to the same conclusion by regarding adsorption as a saturation of the residual valencies. An adsorption layer thicker than one molecule appears to him improbable, because he supposes the forces of chemical valency to act only over very short distances—the maximum action at $0{\cdot}6 \times 10^{-8}$ cm.[2] What picture of adsorption phenomena he obtains in this way has been described in detail earlier (p. 130).

Bakker [3] arrives at higher values for the thickness of the surface layer by considering the surface layers of liquids in contact with gases. His theory cannot be discussed in detail here. Only so much may be remarked, that he starts with van der Waals [4] and Hulshof [5] from the view that the liquid in the surface-layers passes over continuously into the vapour; accordingly he assumes there a series of layers of expanded liquid and compressed vapour, and further assumes them to follow one another as required by the p, v curve of van der Waals. Since he arrives from this point of view at certain probable suppositions concerning the gradient of density $\frac{d\varrho}{dh}$, he is able, on the basis of the equation mentioned on p. 11,

$$\sigma = k \int \left(\frac{d\varrho}{dh}\right)^2 dh,$$

in which the integral must be extended over the thickness of the surface-

[1] *Lenard* (Sitzungsber. d. Heidelb. Akad. d. Wiss., 1914, 28 Abh., Anm. 7, p. 7) would prefer another explanation for the approximate proportionality between radius of the sphere of action and distance between the molecules, namely that "with increasing size of molecule the material filling up of space between the attracting molecules increases." He therefore supposes (Anm. 1, p. 4 of the same paper) that the attraction between two molecules also depends upon whether other molecules are between them or not. As he himself remarks, a certain difficulty of this conception lies in the fact that *van der Waals's* equation is so widely true not only for gases, but also for liquids. It is still more difficult to reconcile with this conception the fact that, according to *Polanyi* (cf. p. 125), even in the adsorption layer of a solid body, in a space therefore in which the attractive force of the solid molecules acts, *van der Waals's* equation may be applied to the adsorbed gas.

[2] *Langmuir*, Journ. Amer. Chem. Soc. **38**, 2247 (1916).

[3] *loc. cit.* p. 11; especially the papers from Zeitsch. f. physik. Chemie, **86**, 129 (1918) onwards.

[4] *loc. cit.* p. 11.

[5] *loc. cit.* p. 11.

layer, to deduce a relationship between thickness, surface tension and gradient of density. Thus in certain limiting cases [1]—if the temperature is a certain fraction of the critical—the thickness of the surface-layer is found to be

$$\Delta = \frac{\sigma}{p},$$

where p is the vapour pressure at the temperature in question. For ethyl ether this temperature is 110·7°, and we get for Δ at this temperature 8·5 $\mu\mu$. Also at other temperatures and for other liquids the thicknesses similarly calculated fall within a range of several $\mu\mu$.

A more general formula allows of the calculation of Δ at various temperatures. The result shows a pronounced increase in the thickness of the surface-layer in the neighbourhood of the critical temperature; for CO_2, for example, Δ increases between −30° and + 20° from 1·5 $\mu\mu$ to 3·5 $\mu\mu$; between + 20° and + 30° from 3·5 $\mu\mu$ to 26 $\mu\mu$.[2]

Experimental Data concerning the Thickness of Surface-Layers

If we review the experiments which permit the thickness Δ of the surface-layer to be calculated, many appear to tell in favour of a considerable thickness. Those may be considered first which relate to the interface liquid—gas, since they also take the first place in theoretical discussions. The quantity Δ may be deduced from the *properties of thin films of liquid*. Striking and quite free from objection are experiments by Rayleigh,[3] which are completely similar to earlier experiments of Frl. A. Pockels.[4] The thickness of oil films spread upon the surface of water was determined, and the dependence of the surface tension of the water covered with oil upon the thickness of the film. The water, upon which a weighed drop of castor oil had been allowed to fall, was contained in a rectangular sheet-iron vessel in which, as described on p. 71, the contaminated surface could be increased or decreased as desired by sliding strips of glass; the oil layer could thereby be made thicker or thinner as desired. The surface tension was determined in relative measure from the weight which just sufficed to tear a round plate away from the surface. Table 97 and Fig. 65 contain the results of such a series of experiments; the thickness τ of the layer of oil is given in $\mu\mu$. The values could always be obtained in the reverse direction.

As we see, the surface tension is not altered by the smallest amounts of oil. Only above a certain thickness of the layer τ_0, about 1·3 $\mu\mu$, does σ fall greatly. From this thickness τ_0 we cannot deduce the thickness of the surface-layer; it only tells us the amount of substance which has any effect at all on the surface tension. After the rapid fall σ gradually becomes constant when a thickness δ of about 5 $\mu\mu$ is reached. δ may be regarded as that thickness from which onwards the layer of oil has the properties of the liquid oil phase in bulk. From δ the thickness of the surface-layer may be calculated. Formerly the opinion was held that δ is twice the thickness of the surface-layer; that in the thinnest possible phase surface we are dealing with two adjacent surface-layers. This is according to Bakker [5] im-

[1] *Bakker*, Zeitschr. f. physik. Chemie, **86**, 133 (1914).
[2] *Bakker*, Zeitschr. f. physik. Chemie, **93**, 171 (1919).
[3] Phil. Mag. (5), **48**, 331 (1899).
[4] Nature, **43**, 437 (1891).
[5] Zeitschr. f. physik. Chemie, **61**, 595 (1908).

TABLE 97

Dependence of the Surface Tension of Water upon the Thickness of a Covering Layer of Oil.[1] Room Temperature

τ in $\mu\mu$.	σ.
0	73·0
1·28	73·0
1·41	72·5
1·53	71·6
1·59	70·7
1·70	68·6
1·78	66·4
1·84	62·0
1·93	57·5
2·08	52·6
2·29	44·2
2·67	35·4
3·04	31·0
4·58	26·6
6·37	24·4
8·17	23·0

probable, since according to his view a surface-layer must necessarily be adjacent to liquid in bulk, in order to be permanent; he therefore assumes a further layer of liquid of the thickness of the sphere of molecular action,

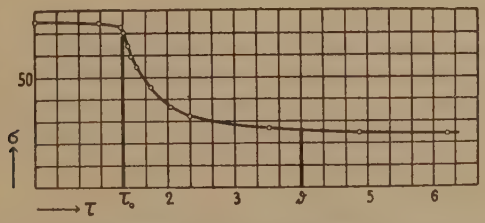

FIG. 65.—Dependence of Surface Tension of Water upon the Thickness of a Layer of Oil upon its Surface.

between the two surface-layers. δ would thus lie between two and three times the thickness Δ of the surface-layer; according to the Rayleigh experiments just given, therefore, between about 1·5 $\mu\mu$ and 2·5 $\mu\mu$.

A large number of measurements are to be found in the literature in which, in a similar manner to that just described for the surface tension, the dependence of a property upon the thickness of an extremely thin phase layer has been investigated. The majority do not go so far as to allow the thickness δ, above which the thin layer of a phase has the same properties as the phase in bulk, to be determined, while they all lead to a value for

[1] The relative values of *Rayleigh* were recalculated to absolute ones by taking into account his statement that the point at which the motion of camphor particles ceases upon a contaminated surface (cf. p. 70) corresponds to $\tau = 2$ $\mu\mu$ and a surface tension of about 55 [cf. also *Rayleigh*, Phil. Mag. (5), **30**, 386 (1890)].

τ_0, viz. to a minimum thickness of the layer in question at which it just makes its influence felt upon the property in question. Of this kind are the numerous measurements of the thinnest films of oils and other substances on water or mercury surfaces. Apart from a large number of older measurements,[1] Devaux,[2] Marcelin,[3] Langmuir,[4] and Labrouste [5] in particular have carried out such experiments. They mostly employed Devaux' arrangement: weighed drops of a solution, say of an oil, in petrol, are allowed to fall upon the water, which is contained in a rectangular photographic dish; the petrol evaporates and leaves behind a thin layer of oil. By pushing the oil back to one side of the surface, and strewing upon the other part a pure powder such as talc (cf. p. 71), the extent of the oil layer can be determined by the receding of the talc border. From the weight of the amount of oil used and the extent of the film, its thickness may be calculated. Values of about 1 $\mu\mu$ were almost always found for the thickness, which correspond to the thickness of one layer of molecules. Thus Marcelin obtained a value of 0·94 $\mu\mu$ for oleic acid, while on the basis of the kinetic theory one of 0·75 was to be expected; for olein Devaux found an observed value of 1·10 $\mu\mu$, Marcelin one of 1·04 $\mu\mu$, as against a theoretical value of 1·12 $\mu\mu$. Marcelin's experiments on camphor are also striking. Around a piece of camphor lying upon a water surface an adsorption layer is formed, as described on p. 98. The talc powder is therefore driven back over a circular surface around it. At given times after the commencement of this driving back of the talc the diameter of the circle is determined, and from the velocity of evaporation of the camphor—measured over longer periods—the amount evaporated during the short period of the experiment; from these data the thickness of the adsorption layer can be calculated. The result was 0·4–0·5 $\mu\mu$, while the theory required 0·6 $\mu\mu$.

Quite similar are the results of other observations: the value of τ_0 in the above-discussed curve of Rayleigh, the thickness of the surface films of substances such as peptone, albumin, and others which were still just solid,[6] the thinnest layer of mercury, which just acts catalytically upon the decomposition of hydrogen peroxide,[7] and others. It is important that in the cases in which by pushing together the surface-layer solid films can be obtained, these always disappear reversibly upon the surface being enlarged again.

Marcelin found the thickness of an adsorption layer which was in equilibrium with lenticular oil drops upon a water surface to be several times greater than the thinnest oil layers above referred to, about twice or three times as thick. The thinnest oil film which prevents the dancing of camphor particles on a water surface is thicker. For according to Devaux [8] they dance upon a water surface which is coated with the thinnest possible layer of oil almost as well as on pure water. Only when the oil film is

[1] See *Sohncke*, Wied. Ann. **40**, 345 (1890); *Röntgen, ibid.* **41**, 321 (1890); *Rayleigh*, Proc. Roy. Soc. **47**, 364 (1890); **48**, 128 (1890); Phil. Mag. (5), **31**, 362 (1897); *Oberbeck*, Wied. Ann. **49**, 366 (1893); *K. F. Fischer, ibid.* **68**, 414 (1899), and others.

[2] *loc. cit.* p. 71.

[3] Ann. d. physique (9), **1**, 19 (1914).

[4] *loc. cit.* p. 71.

[5] Compt. rend. **157**, 44 (1913); **158**, 627 (1914); **159**, 306 (1914). There are also experiments upon the influence of temperature on such layers.

[6] *Devaux*, Journ. de phys. (4), **3**, 450 (1904); *Metcalf*, Zeitschr. f. physik. Chemie, **52**, 1 (1905); *Langmuir, loc. cit.* 71.

[7] *Bredig* and *Weinmayr*, *Boltzmann*-Festschrift 1904, p. 839.

[8] Journ. de phys. (5), **2**, 703 (1912).

pushed together to about half its extent, so that its thickness is about 2·2 $\mu\mu$, does the motion cease. Rayleigh [1] also found under the same conditions a thickness of 2 $\mu\mu$.

Conclusions as to the thickness of the surface-layer have frequently been drawn from the thickness of the thinnest soap solution films, the so-called black films, which will be discussed later (p. 794). It appears to me questionable whether this is allowable. For their behaviour as compared with the soap solution is entirely in favour of the view that they are chemically different from it. Nevertheless, physicists have repeatedly neglected these chemical differences and regarded the thickness δ of such a thinnest black soap lamina as corresponding to the thinnest possible phase layer. Thus Bakker [2] calculates upon the basis of experiments by Johonnott,[3] who found a minimum thickness $\delta = 6$ $\mu\mu$, a $\Delta = \frac{1}{3}\delta = 2$ $\mu\mu$. This, as has been said, hardly appears to be justified.

Experiments, in which a thickness δ is plainly to be distinguished along with a τ_0, are met with in the investigation of the behaviour of solid metals in their dependence upon the thickness of the layer. Almost all these experiments are open to the objection that the layers of metal are probably not continuous but disperse. This applies least to the experiments of Oberbeck.[4] He produced layers as uniform as possible of suitable metals (Zn, Cd, and Cu) upon a platinum electrode, and followed the rate of change of the potential of this electrode against another platinum electrode. At first the E.M.F. is the same as a full electrode of the same metal would show. After a definite time a rapid decline in the E.M.F. takes place. Here either the metal has no longer the same properties as in the mass, or the potential of the platinum makes itself felt through the layer. One is therefore not certain as to what fraction one should take of this thickness—which can be calculated from the quantity originally present, the amount dissolved up to the critical time, the density, and the size of the electrodes. As regards the latter possibility, that the platinum makes itself felt through the layer, the thickness would in that case be equal to the sphere of action. The numbers obtained by Oberbeck lay between 1 and 3 $\mu\mu$.

Instead of the E.M.F., the conductivity of such thin metallic laminæ has been investigated, and also the change in phase of reflected light. Thus Moreau [5] found from the conductivity of electrolytically deposited layers of nickel the smallest thickness, at which they had the properties of the metal in mass, to be 22 $\mu\mu$. This would give, taking the same fraction as in the case of liquid phase surfaces, a $\Delta = 7$ $\mu\mu$. Vincent [6] obtained by similar experiments with silver mirrors, and Patterson [7] with platinum films produced by cathode deposition, values of $\delta = 50$ and 7 $\mu\mu$ respectively, and Δ therefore = about 15 and 2 $\mu\mu$. It may be objected to these measurements that such layers are practically certain to be disperse (cf. p. 787). The same objection may be raised to the experiments of O. Wiener [8] with silver mirrors, in which he followed the change in phase of the light upon

[1] Proc. Roy. Soc. **47,** 366 (1890); see also Phil. Mag. (5), **30,** 386 (1890).
[2] Zeitsch. f. physik. Chemie, **61,** 603 (1908).
[3] Phil. Mag. (5), **47,** 501 (1899); (6), **11,** 746 (1906).
[4] Wied. Ann. **31,** 193 (1887).
[5] Journ. de phys. (3), **10,** 478 (1901).
[6] Ann. de chim. et de phys. (7), **19,** 421 (1900).
[7] Phil. Mag. (6), **4,** 652 (1902).
[8] Wied. Ann. **21,** 629 (1887); see also *Königsberger* and *Benda,* Ann. d. Physik (4), **26,** 763 (1908).

reflection and its dependence upon the thickness, quite apart from the new circumstance that the critical values of the thickness are not independent of the wave-length of the light. τ_0 was very distinctly differentiated from δ. At a thickness $\tau_0 = 0{\cdot}2\ \mu\mu$ the optical behaviour could not be distinguished from that of the mica plate which carried the layer; at one of 10–12 $\mu\mu$ it was that of the metal in bulk.

From adsorption experiments the thickness of the surface-layer may be estimated, if the size of the adsorbing surface, the amount and density of the adsorbed substance in the adsorption layer, are known. On account of the internal surface the determination of the surface area is difficult with most adsorbents, and as regards the density, uncertainty exists on account of the gradient of density present at the surface (cf. p. 123). It must further be noted that with solid adsorbents one does not determine the thickness of the whole surface-layer, but only that of the part which reaches into the space filled with gas or liquid; after what was said on p. 307 this would therefore be about half the value of Δ. Only the following observations may be given. Fink [1] found that at a platinum surface of 4,600 sq. cm. at 248° 0·011 grammes of SO_3 were adsorbed; if we assume somewhat arbitrarily a density of 2, we get a thickness for the layer $\frac{\Delta}{2} = 1{\cdot}2\ \mu\mu$. This value would rather be too small than too large, since besides SO_3 also O_2 and SO_2 were adsorbed. Ihmori [2] determined with a very delicate balance the increase in weight experienced by various materials in moist air. From the best experiments, for example, with an ignited platinum foil in water vapour below saturation point, the amount of water adsorbed was so small that the thickness of the layer was certainly not greater than $0{\cdot}2\ \mu\mu$. This would tell in favour of a unimolecular thickness of the layer. Under less pure conditions thicknesses between 3 and 10 $\mu\mu$ were obtained on bright metals (nickel, brass, steel), and still larger ones on quartz and glass. Numerous older and newer numerical data concerning the thickness of the layer of water and other liquids on glass and other silicates are also distinctly large and vary greatly. Thus, for example, Parks [3] calculates from his own and other experiments values between 70 and 406 $\mu\mu$. It is in this case very doubtful whether the water is limited to the surface and does not penetrate considerably below it owing to chemical interaction.

Langmuir, on the other hand, as will be discussed in further detail later (p. 317), calculates from Szyszkowsky's formula the amounts adsorbed at the surface in aqueous fatty acid solutions at adsorption saturation, and arrives at good agreement with other results when he assumes that the adsorption layer consists of only one layer of molecules of the fatty acid.

If we review the results of experiment and theory, it will be very difficult to come to a decision. It appears to me to be without doubt, especially after what will be discussed in the next section, that unimolecular layers frequently occur as boundary layers and play an important part. Whether they must be necessarily or generally postulated appears to me to be questionable. In the case of oil layers on water there are cases in which the layer is a few molecules thick, certainly more than one. And the possibility must also be considered that further molecular layers of the water, which

[1] "Die Kinetik der Kontaktschwefelsäure." Diss., Leipzig, 1907, p. 52.
[2] Wied. Ann. **31**, 1006 (1887) and *E. Warburg* and *Ihmori, ibid.* **27**, 481 (1886).
[3] Phil. Mag. (6), **5**, 517 (1903).

are adjacent to the possibly unimolecular oil layer, are so altered that they must be counted as part of the surface-layer.

Perhaps much that is contradictory would become clear if, as also Langmuir points out, one were to take the roughness of the surface more into account. If the radius of molecular action were not strictly limited to one molecular diameter, but the attractive force fell off so rapidly that the further action is extremely small, then it would be comprehensible why unimolecular layers are so frequent and so much preferred. The surface of a solid adsorbent could, however, be so rough that very frequently, in exceedingly small cavities in the surface, that part of the sphere of molecular action which reaches beyond the thickness of a molecule might be superimposed from opposite walls, and in this way a sensible attraction might be brought about beyond the first layer of molecules.

But a great difficulty still appears to me to remain when we attempt to explain electrokinetic phenomena. The thickness of the diffuse double layer was already discussed earlier (p. 254), with the result that in dilute solutions values of 5–10 $\mu\mu$ should frequently occur. The great influence which dissolved substances exert on account of their adsorbability—we are however dealing with a polar adsorption—drives us to the assumption that the adsorption layer is not confined to one layer of molecules, but also penetrates more deeply. The possibility exists that one might have to distinguish in this respect between polar and apolar adsorption, and that in the case of the former, which is essential to electrokinetic phenomena, thicker adsorption layers occur than in the case of the latter ; a reason for this is, however, not immediately evident.

Later (p. 719), phenomena in connexion with gels will be described, which are also hardly to be understood without the assumption of a larger sphere of molecular action, and these would again lead to adsorption layers containing more than one molecular layer.

The Fine Structure of Surface-Layers

Quite independent of the question as to the probable or greatest possible thickness of the surface-layer appears to me to be the fact that layers occur which contain only one molecule, and that, for example, the thinnest layers of oil and other substances on water are examples of this kind. Langmuir [1] and Harkins and his co-workers [2] have succeeded in drawing noteworthy conclusions from the behaviour of such unimolecular layers.

We already (p. 69) touched upon the view of these authors, that in the case of molecules containing both strongly and weakly saturated groups, such for example as the fatty acids, the completely saturated group in the surface is directed outwards, the one rich in residual valency inwards. This is, in their opinion, very decidedly the case, when a thin layer one molecule thick, say of a difficultly soluble fatty acid, is spread out upon water. The group COO will turn itself with its residual valencies towards the water, the saturated CH_3 group, on the other hand, outwards ; the molecules stand in this case also—as opposed to the case of the adsorption of a soluble fatty acid in dilute solution (cf. p. 68)—with their length at right-angles to the surface.

[1] Journ. Amer. Chem. Soc. **38**, 2221 (1916) ; **39**, 1848 (1917).

[2] *Harkins, Brown* and *Davies*, Journ. Amer. Chem. Soc. **39**, 354 (1917) ; *Harkins, Davies* and *Clark, ibid.* **39**, 541 (1917) ; *Harkins, Clark* and *Roberts, ibid.* **42**, 700 (1920) ; *Harkins* and *Cheng, ibid.* **43**, 35 (1921).

If this is correct, then the space taken up in the surface layer by one molecule of fatty acids of different molecular magnitude should be equally great; it would always be a question of the surface occupied by the CH_3 group, and towards the water only COO groups are turned. This surface may be determined if we know the greatest possible surface over which a given amount of fatty acid can be distributed; one only needs to divide this largest possible surface by the number of molecules present, as obtained from the product of the weight of acid employed and Avogadro's number N. In the following table is found, according to Langmuir, firstly the surface ω_M occupied by one molecule, secondly the square root of this surface $b_M = \sqrt{\omega_M}$, which corresponds to the distance between the molecules in the surface-layer; further, l_M, the length of the molecules, which may be calculated from the molecular volume and the quantity b_M; finally l_C, the distance between the carbon atoms, if the length l_M is regarded as a straight line. In actual fact, ω_M is practically equal for palmitic, stearic, and cerotic acids, as required by theory. In the case of tristearin it is about three times as great, in agreement with the fact that all three fatty-acid chains end in a CH_3 group in the surface. The same contrast exists between oleic acid and triolein. That oleic acid has ω_M about double that of the saturated fatty acids would be explained by the two groups rich in residual valencies—the carboxyl group and the double bond—lying inwards towards the water; the molecule is bent as it were, and a CH_3 group, as well as a CH_2 group, lie outwards in the surface.

TABLE 98

Measurements of Molecules, as deduced from their Behaviour on Surface Layers

Substance.	$\omega_M \cdot 10^{16}$	$b_M \cdot 10^8$	$l_M \cdot 10^8$	$l_C \cdot 10^8$.
Palmitic acid, $C_{15}H_{31}COOH$	21	4·6	24	1·50
Stearic acid, $C_{17}H_{35}COOH$	22	4·7	25	1·39
Cerotic acid, $C_{25}H_{51}COOH$	25	5·0	31	1·20
Tristearin, $(C_{18}H_{35}O_2)_3C_3H_5$	66	8·1	25	1·32
Oleic acid, $C_{17}H_{33}COOH$	46	6·8	11·2	0·62
Triolein, $(C_{18}H_{33}O_2)_3C_3H_5$	126	11·2	13	0·69
Trielaïdin, $(C_{18}H_{33}O_2)_3C_3H_5$	120	11·0	13·6	0·72
Cetyl palmitate, $C_{15}H_{31}COOC_{16}H_{33}$	23	4·8	41	2·56
Myricyl alcohol, $C_{30}H_{61}OH$	27	5·2	41	1·37

Hence the length is found to be half as great as in the case of the saturated acid. The behaviour of cetyl palmitate leads to a curious conclusion. Since ω_M is just as great as for the saturated fatty acids, the CH_3 group should again be directed outwards, and the COO group towards the water. But the length is different from that of the acids named. One might be tempted to conclude from this that the C atoms of the carbon chain do not lie upon a straight line, but upon a zig-zag, so that the total length is variable. In agreement with this is the fact that the distance between the C atoms, calculated from the total length, the quantity l_C, is smaller than one would expect. For in the case of diamond, in which these atoms may be considered to be as closely packed as possible,[1] a greater value, $1{\cdot}52 \times 10^{-8}$

[1] *Marx*, "Handbuch der Radiologie," Leipzig, 1919, Bd. V, p. 556.

cm., is obtained for their distance apart. The values of l_M show us that the fatty acid molecule, for example, may actually be regarded as long and narrow. It is about five times as long as broad.

For the results of further work in this direction the reader is referred to Langmuir's experiments, who has also determined with a modified Devaux arrangement the thinnest layers of solids. It may be added that according to him there are reasons for believing that in the case of aromatic substances the benzene rings lie flat in the surface.

Langmuir confirms this view in yet another way. He assumes that the state of adsorption saturation, which one can probably always reach in concentrated solutions of soluble fatty acids (see p. 182), again simply means that the surface-layer consists solely of fatty acid molecules which, since they are closely packed, again have the CH_3 group outwards, and the COO group inwards. Since saturation has not been directly measured for aqueous solutions, he determined the amount that could then be adsorbed from Szyszkowsky's formula, as has already been done on p. 113. If we substitute in the Gibbs adsorption equation

$$\mathfrak{a} = -\frac{c}{RT}\frac{d\sigma}{dc}$$

the expression

$$-\frac{d\sigma}{dc} = \mathfrak{b}\sigma_M\frac{1}{c+\mathfrak{c}}$$

(see equation (3) p. 113) from Szyszkowsky's formula, then we get

$$\mathfrak{a} = \frac{\mathfrak{b}\sigma_M}{RT}\frac{c}{c+\mathfrak{c}}.$$

For large values of c adsorption saturation is reached, $\mathfrak{c}$ may be neglected as compared with c, and we get for the amount adsorbed

$$\mathfrak{a}_\infty = \frac{\mathfrak{b}\sigma_M}{RT}.$$

Since $\mathfrak{a}_\infty$ refers to the amount adsorbed per square centimetre, we only need to multiply it by N in order to get the number of molecules per square centimetre, and thus also

$$\omega_M = \frac{1}{\mathfrak{a}_\infty N},$$

i.e. the surface occupied by a single molecule.[1] The values so found actually agree with those obtained by other means, as given in Table 98. Thus for acetic acid, according to Milner's measurements (see p. 63), we get $\omega_M = 31 \times 10^{-16}$ (instead of 23×10^{-16} for the fatty acids in Table 98), for isobutyric acid (Table 20, p. 62) we get $30{\cdot}6 \times 10^{-16}$.

This view of Langmuir's allows us, it may be remarked, to refer to residual valency the phenomena of the spreading of liquids, as interpreted on p. 96 on the basis of interfacial tensions. According to him, those liquids spread out, which can turn a group rich in residual valency towards the water, as can the fatty acids and such like; these are the substances which, according to what was said earlier, spread on account of the low interfacial

[1] *Langmuir* points out that in the other limiting case, that of very slight adsorption, an equation may be deduced from *Gibbs's* formula which is similar to *van't Hoff's* law in solutions. The product of a tension into the surface occupied by one mol is equal to RT.

tension σ_{AB}. On the other hand, the pure hydrocarbons do not spread, since they are devoid of such a group. For the same reason the interfacial tension is so great that the drops lie lenticularly upon the surface.

According to recent experiments of Kruyt and van Duin,[1] the directed position of the molecules in adsorption probably also plays an important part in reactions which take place in an adsorption space. It can for example produce the effect that, although two substances which react with one another are adsorbed by an adsorbent, a reaction between them is not accelerated, because the two reacting groups are so directed that they cannot easily react with one another; an acceleration, on the other hand, is observed when they also come easily into contact with one another on account of their orientation in the surface.

B. THE KINETICS OF THE FORMATION OF A NEW PHASE

It is important for the production as well as for the stability of colloidally disperse systems that one does not as a rule start from two pre-existing phases and distribute the one exceedingly finely in the other, but usually allows the second to be formed in a colloidally disperse form in a previously homogeneous phase. That this can be so conveniently carried out is principally due to the fact that phenomena of supersaturation occur so frequently and so easily. From a supersaturated vapour there arises a mist under various conditions—by supercooling, by dust, by carriers of electricity; from a supersaturated solution a sol is formed. For colloid chemistry the transition from the unstable condition of supersaturation to the stable two-phase state is particularly important, hence the phase rule proper, which is concerned with the equilibrium between phases, plays here only a subsidiary part. On the other hand, much depends upon the velocity with which the transition takes place, therefore upon *the kinetics, of the formation of a new phase.*

In the formation of mist and smoke from a supersaturated vapour the phenomena are such that they are most usefully discussed in connexion with these colloidally disperse systems themselves, since the greater number of examples must be taken from colloid chemistry.

It is otherwise in the case of the transition of a liquid phase to a solid. Here most experimental results regarding the kinetics have been obtained on non-disperse systems, so that it would appear proper to deal with them here. It is a question first of all of the production of a solid phase from a supercooled molten mass. This crystallization of a supercooled melt is however of little direct importance for colloid chemistry. But it allows of a clear definition of the quantities which can be measured and of the phenomena which come into question. Crystallization from a supersaturated solution is important for colloid chemistry, but less easily treated.

The Rate of Formation of Nuclei in Supercooled Melts

If a molten pure substance is cooled below its freezing-point, it may be supercooled to a greater or less degree. The further the temperature falls below the freezing-point, the sooner does the melt commence to crystallize from one or several points. In a certain range of temperature below the melting-point this tendency to crystallization is usually so great that it is difficult or impossible to prevent it. If one can reach lower temperatures

[1] Rev. d. trav. Chim. d. Pays-Bas, **40**, 249 (1921).

quickly, however, this tendency disappears again ; the melt becomes viscous and solidifies to a glass.

Molecular-kinetic conceptions, as first developed by de Coppet,[1] and supported in a similar form by Tammann,[2] are most in accordance with the observed results. The molecules of the supercooled liquid, the velocities of which correspond to the mean state of motion, are certainly not inclined to take their places in the space lattice of the crystal, otherwise a rapid formation of crystals would set in immediately below the freezing-point. If indeed at all, only a small fraction of the molecules is capable of forming *crystallization centres* or *nuclei*, from which further crystallization proceeds.

In what fashion the kinetic energy of the molecules affects their transition from one phase into another is clearly seen from experiments by Knudsen.[3] Knudsen generated a jet of gas, e.g. of mercury vapour ; that is, he allowed the gas molecules to enter a vacuum through a narrow opening, so that only those molecules moving parallel to the axis of the opening could fly through, and examined whether or no, and how far, they were thrown back on impingeing on a wall. If no rebound takes place, the mercury molecules remain upon the cooled wall of impact exactly opposite the opening out of which they came. If they rebound, they also form a deposit upon the walls around the area of impact. It could be shown that mercury molecules are not thrown back by a mercury surface, but remain adhering after the first impact. When however they struck a wall of glass, this had to be cooled to $-183°$ in order to secure quantitative adhesion of the mercury. At a temperature of $-78°$ the greater part rebounded. The decisive temperature was different for different substances. When copper molecules were examined instead of mercury, they were found to adhere to glass already at temperatures between $+350°$ and $+575°$.

This kind of adhesion, as Knudsen rightly points out, is doubtless a necessary condition for the production of nuclei. The kinetic energy of the molecules on collision must not exceed a certain small value. Hence also in supercooled melts only molecules with a sufficiently low kinetic energy will be able by sticking together to form a minute crystal and so act as nuclei. Whether besides this requirement regarding the kinetic energy other conditions also must be fulfilled by the molecules in question is not yet decided, but it is not improbable ; thus, for example, it may be that only molecules with quantum orbits altered in some way are able to form a crystal nucleus on collision.

It may be regarded as certain that at still lower temperature the conditions for the production of nuclei become less favourable again, since the decrease in molecular motion as the absolute zero is approached, and the increase in viscosity, are unfavourable to the combination of suitable molecules to nuclei.

We define the *velocity of formation of nuclei* as the number of nuclei or centres of crystallization formed per unit of time in unit weight of supercooled liquid ; this quantity is called by de Coppet and Tammann the *power of spontaneous crystallization* ; with a fall of temperature it must pass

[1] Ann. de chim. et de phys. (5), **6**, 275 (1875) ; (8) **10**, 457 (1907).

[2] "Kristallisieren und Schmelzen," Leipzig, 1903, p. 148 *et seq.*

[3] Ann. d. Physik (4), **50**, 472 (1916). The later, in part unpublished investigations of *Volmer* upon crystallization from metallic vapours [*Volmer*, Zeitschr. f. Physik, **5**, 31 (1921), *R. Gross* and *Volmer*, *ibid.* **5**, 188 (1921), *Volmer* and *Estermann*, *ibid.* **7**, 1, 13 (1921)], will considerably advance in this connexion both the theory of the formation of nuclei, as also probably that of the velocity of crystallization.

through a maximum. A pictorial representation on the basis of the Maxwell distribution curve, which is similar to that of de Coppet, makes this plain (see Fig. 66). As is well known, in this curve of distribution the velocities of the molecules v are plotted as abscissæ, as ordinates the relative probabilities

$$y = \frac{4}{\sqrt{\pi}a^3} v^2 e^{-\frac{v^2}{a^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

with which the particular velocity v occurs, a being the most probable velocity. The molecules forming nuclei have a lower velocity than that of the average, and it will be possible to delimit a certain range of active velocities. The meaning of the upper limit v' is clear from the above-mentioned experiments of Knudsen; the lower limit v'' depends, as has been said, upon the increase of viscosity and decrease of molecular motion with fall of temperature. The area between v' and v'' is proportional to the number of molecules forming nuclei. If the temperature falls the curve is displaced towards the left. The area will increase in size, the number of molecules able to form nuclei increases. It reaches a maximum, when the area between v' and v'' comprises the maximum of the curve. The number decreases again when after a further fall of temperature the area comes on the other side of the curve; there molecules are able to form nuclei whose velocity exceeds the most probable velocity.

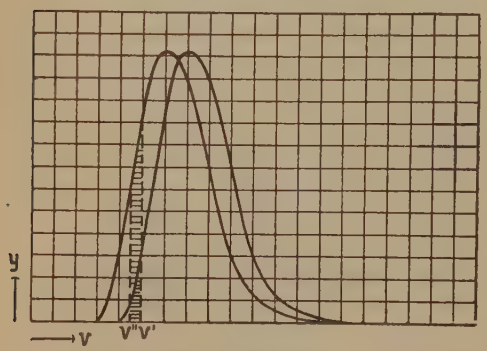

Fig. 66.—Velocity of Formation of Nuclei and Maxwell's Distribution Curve.

Tammann [1] has actually proved that the velocity of formation of nuclei passes through a maximum in this way as the temperature falls, and the supercooling therefore increases. In Fig. 67 the rate of formation of nuclei for piperine is illustrated; as ordinates we have the velocities of formation of nuclei, as abcissæ the temperatures. As velocity of formation of nuclei we have the number of nuclei which were detected under definite experimental conditions. As regards its measurement, one can, at the temperature of the maximum and above it, count directly the number of nuclei in a layer of the supercooled melt pressed between two glass plates. In the region of lower temperatures the nuclei usually cannot be recognized, because the velocity of crystallization has become so small that visible crystals are not formed sufficiently fast from the nuclei. Tammann then makes use of the following artifice. He cools the melt for a definite time down to the low temperature, and then warms it up quickly to a somewhat higher temperature, so that the velocity of crystallization is already sufficiently large, but the velocity of formation of nuclei remains small. The

[1] Zeitschr. f. physik. Chemie, **25**, 442 (1898). "Kristallisieren und Schmelzen," p. 151. Also in the supercooled metallic melts of antimony and bismuth *Bekier* [Zeitschr. f. Anorg. Chemie, **78**, 178 (1912)] found similar maxima of the rate of formation of nuclei.

nuclei formed at the lower temperature are "developed," as it were, by allowing them to grow into visible crystals at a higher temperature. Another method used by Tammann [1] consists in generating a temperature gradient in a tube filled with the supercooled melt. The point at which most crystals appear corresponds to the temperature of the maximum velocity of formation of nuclei.

The steep rise in the Maxwell distribution curve (Fig. 66) has the consequence that the velocity of formation of nuclei also increases very greatly with increased supercooling. This suggested the view first considered by W. Ostwald [2] that below the freezing-point we have first a *metastable* region, in which no crystals are formed spontaneously; a *metastable boundary* divides this from the *labile* range of temperature, in which crystallization necessarily occurs. Miers and Miss Isaac [3] believed that they could regard their experiments on supersaturated solutions—in which similar conditions in this respect are to be reckoned with—as confirming the existence of a metastable boundary. For they found that while at low degrees of supersaturation at most a few centres of crystallization were formed on the surface, at a comparatively little greater supersaturation a cloud of the finest crystals suddenly filled the interior of the liquid. But a sudden rise of this sort in the velocity of formation of nuclei is quite to be expected on the basis of the distribution curve. Just as there is here a *threshold value* of the temperature, so we also find similar threshold values in other phenomena which may be correspondingly referred to the curve of distribution (cf. p. 445).

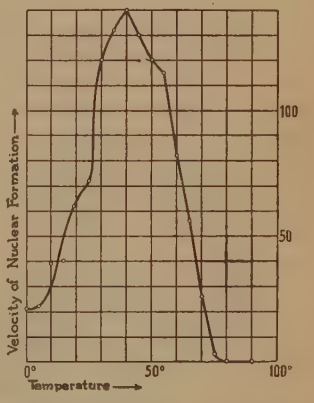

FIG. 67.—Dependence of Velocity of Nuclear Formation upon Temperature.

In favour of the kinetic interpretation there are also other results; especially the great sensitiveness to foreign substances, both towards those in solution and those existing in the melt as solid particles. Experiments in this direction are not yet sufficiently extended to allow of anything trustworthy being said as to which properties determine this influence. Both the number of nuclei and the temperature of the maximum may be altered. Tammann [4] found, for example, that with supercooled betol, salicylic acid and cane sugar diminish the number of nuclei. Anisic acid increases it; glass powder diminishes it to zero. Emery and rock-crystal powders increase it. There is no close connexion between maximum velocity of formation of nuclei and viscosity. Also the form and appearance of the nuclei change with the nature of the foreign substances added.[5]

The great sensitiveness to foreign substances makes it more difficult to

[1] Zeitschr. f. anorg. Chemie, **87**, 248 (1914).

[2] Zeitschr. f. physik. Chemie, **22**, 302 (1897); Lehrb. d. Allgem. Chemie, Leipzig, 1902, Vol. II, p. 773; see also p. 751.

[3] Journ. Chem. Soc. **89**, 413 (1906); **93**, 927 (1908); Miss *Isaac, ibid.* **93**, 384 (1908).

[4] *loc. cit.* p. 320.

[5] *Hartmann*, Zeitschr. f. anorg. Chemie, **88**, 128 (1914).

judge upon what properties of the pure liquid the velocity of formation of nuclei and the position of the maximum, in other words the possible supercooling, depend. A general review of the behaviour of a large number of substances is found in the above-mentioned investigation by Tammann.

S. W. Young [1] attempted to follow the well-known effect of friction upon velocity of formation of nuclei quantitatively by stirring a supercooled liquid under comparable conditions, or allowing a small hammer, which could be variously loaded, to fall upon an anvil in the liquid. The experiments so far available do not allow of any decision as to whether it is a question of the purely mechanical action of the blow, or whether the material of which hammer and anvil are made has also a direct influence. In the latter case the action could be referred to that of powdered solid mentioned above. In any case the result was obtained that crystallization of water could already be brought about in this manner at $\frac{1}{10}°$ of under-cooling. This is a further proof of the non-existence of a metastable range in the sense that in it crystallization can only be brought about by crystalline nuclei introduced from without.

The Velocity of Formation of Nuclei in Supersaturated Solutions

In supersaturated solutions matters are quite similar as regards the velocity of the formation of nuclei. The same kinetic considerations may also be applied. Only here we have a two-fold variability: we can lower the temperature at given supersaturation, or increase the supersaturation at a given temperature. That in the formation of hydrates, for example, the molecules of the solvent have to enter into the nuclei does not necessarily make the conditions for the formation of a nucleus more difficult, since one may assume as a rule that the water molecules are contained in the colliding solution molecules or ions. Here also we have in the immediate neighbourhood of saturation a threshold within which the probability of crystal formation is extremely small. At higher supersaturation the velocity of formation of nuclei increases very rapidly.

In the case of supersaturated solutions we have further to reckon with the fact that the size of the nuclei is also dependent upon the temperature and degree of supersaturation. For according to the considerations on p. 154, a small crystal, such as a nucleus, has a higher solubility than a larger crystal; it will therefore only be stable at all above a certain degree of supersaturation; at a lower one it will dissolve, at a higher it will grow further. In order to obtain a quantitative conception of this relation, we must discuss with W. J. Jones and J. R. Partington [2] the radius of a nucleus (assumed to be spherical) as a function of solubility and temperature according to the equation (cf. p. 155)

$$\log \frac{L_\omega}{L} = \frac{2\sigma M}{RT\varrho r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The radius r of the crystal nucleus is in equilibrium with the increased solubility or supersaturation L_ω and the temperature of supersaturation T. In considering the change in this equation due to temperature, we must

[1] Journ. Amer. Chem. Soc. **33**, 148 (1911); *S. W. Young* and *R. J. Cross*, *ibid.* **33**, 1375 (1911); *S. W. Young* and *van Sicklen*, *ibid.* **35**, 1067 (1913).

[2] Zeitschr. f. physik. Chemie, **88**, 291 (1914).

remember that L is also a function of the temperature. W. J. Jones and J. R. Partington expressed this by the equation

$$\log L = \frac{u_0}{RT} - \frac{a}{R}\log T + k \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here u_0 is the heat of solution at absolute zero, a is a quantity depending on the specific heat, k is the integration constant We have therefore

$$L_\omega = e^{\left\{\frac{2\sigma}{RT\rho r} + \frac{u_0}{RT} - \frac{a}{R}\log T + k\right\}} \quad . \quad . \quad . \quad . \quad (3)$$

If this formula is compared with one holding for a temperature $T + dT$ we arrive at a differential equation

$$-dT\left\{\frac{1}{T} + \frac{k_1 r}{T} + k_2 r\right\} - \frac{dr}{r} = 0 \quad . \quad . \quad . \quad . \quad (4)$$

In this

$$k_1 = \frac{u_0 \varrho}{2\sigma} \text{ and } k_2 = \frac{a\varrho}{2\sigma}.$$

Now a may be neglected compared with u_0 and hence k_2 compared with k_1, so that by integrating (4) we get

$$T = C\left\{1 + \frac{1}{k_1 r}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where C is an integration constant. If the heat of solution u_0, as is usually the case, is negative, then k_1 is negative, hence

$$1 + \frac{1}{k_1 r} < 1.$$

If then the radius of the particle r decreases, T also decreases according to (5); that is, with negative heat of solution a nucleus which is only just stable in the solution, decreases in size when the temperature falls (and when the supersaturation consequently increases).

In such solutions therefore the tendency to crystallization is extremely small at low degrees of supersaturation. The smaller nuclei, which could form comparatively easily, are unstable and dissolve again immediately; the larger, which are stable, are not readily formed on account of their size. As the temperature falls the conditions become more and more favourable; not only because the number of molecules with small kinetic energy becomes smaller, but also because smaller and easily formed nuclei are stable and do not redissolve quickly. The increase in the velocity of formation of nuclei will therefore be extremely steep, as is indeed shown by the experiments of Jaffé [1] and of Miers and Miss Isaac.[2]

Curious relationships should occur with positive heats of solution. We then have

$$1 + \frac{1}{k_1 r} > 1,$$

that is, as the nuclear size decreases the temperature of supersaturation increases. Two influences thus oppose one another; falling temperature favours the formation of crystals, since the kinetic energy becomes less; on the other hand a falling temperature hinders crystallization, because the stable nucleus increases in size; the converse holds good for a rising tem-

[1] Zeitschr. f. physik. Chemie, **43**, 565 (1903).
[2] *loc. cit.* p. 321.

perature. In the case of an aqueous calcium butyrate solution a behaviour of this kind was found by Miss M. Jones and J. R. Partington [1]; a solution saturated at 18° heated under paraffin oil to 50° deposited crystals at 42°.

From equation (1), p. 322, the so-called inoculation threshold may be calculated, that is, the size of crystal which is necessary for a crystal nucleus to induce crystallization in a supersaturated solution. As long as the r of the crystal is smaller than that required according to equation (1) by the existing supersaturation, it dissolves; crystallization only occurs when r is large enough to satisfy the equation. Johnsen [2] calculates experiments by W. Ostwald [3] on sodium chlorate from this point of view, whereby, however, since the value of σ for sodium chlorate is not known, he substitutes a value found approximately for gypsum by Hulett (cf. p. 155). There results a volume for the smallest crystal of about 10^{-11} c.c., which agrees in order of magnitude with Ostwald's measurements.

The same sensitiveness of the velocity of formation of nuclei to dissolved foreign substances, and to solid particles, occurs also in solution. Thus Jaffé [4] found that the threshold value for supersaturated aqueous solutions of saltpetre decidedly increased when he filtered the solution frequently and carefully.

This is one of several circumstances which at present make it impossible to trace any connexion between chemical constitution and the power of a substance to form more or less readily supersaturated solutions. Other circumstances preventing this connexion from being traced are the various little-known influences to which crystallization is subject, for, quite apart from the kinetic quantities involved, there are also the conditions determining the size of the smallest nuclei capable of existence. With supersaturated solutions, as with supercooled melts, the capacity of the solid substance to crystallize in various forms may be of considerable importance. Very frequently it is the unstable form that separates by preference on spontaneous crystallization. To mention only cases which have been investigated with particular care: according to de Coppet [5] the unstable heptahydrate separated from supersaturated sodium sulphate solutions long before the stable decahydrate, and according to Jaffé in a potassium nitrate solution an unstable rhombohedric form appears instead of the stable rhombic one. This is at first surprising, since the less stable form has the greater solubility and lower melting-point. De Coppet gives the following explanation of this behaviour. The content of free energy is greater in the unstable form than in the stable. Hence molecules of greater kinetic energy can take part in the formation of the unstable form than in that of the stable. Since at a temperature corresponding to a smaller supercooling or supersaturation the molecules with greater kinetic energy are more numerous than at a lower temperature (see p. 320 and Fig. 66), the probability of the formation of the unstable form is at first also greater, and this form occurs first after supercooling or supersaturating. Herein would also lie the explanation of Ostwald's so-called law of stages, according to which the formation of the unstable form is generally preferred.[6]

[1] Journ. Chem. Soc. **107**, 1019 (1915).
[2] Zentralbl. f. Min. Geol. u. Pal. 1917, p. 87.
[3] Zeitschr. f. physik. Chemie, **22**, 289 (1897).
[4] *loc. cit.* p. 323.
[5] *loc. cit.* p. 319.
[6] That pronounced exceptions occur, and can do so in accordance with the kinetic theory, must not be overlooked. Thus from supersaturated aqueous Na_2CO_3 solutions the labile heptahydrate seldom separates; ice, mono- and deca-hydrates are preferred. [*B. M. Jones*, Journ. Chem. Soc. **95**, 1672 (1909)].

The Velocity of Crystallization of Supercooled Melts

A second kinetic quantity independent of the velocity of formation of nuclei is the *velocity of crystallization* ; the velocity with which crystal nuclei once formed grow further in a supercooled melt or supersaturated solution. Every kind of crystal face has its own velocity of crystallization (at right-angles to the surface), and this velocity depends in a characteristic manner for each kind of face upon the temperature, upon foreign substances, and so on. Nacken [1] has recently succeeded in measuring the velocity of crystallization of different faces with salol, employing, however, particular experimental conditions. He followed the crystallization of partly melted crystals between cover glasses under the microscope. The velocities of crystallization were indeed very different, and depended upon the temperature in different ways.

Apart from these experiments, only the so-called *linear velocity of crystallization* has hitherto been measured. With the aid of a procedure due to Gernez [2] it was closely investigated by Tammann [3] and his pupils. The procedure is as follows: The supercooled melt is sucked into a straight or U-shaped capillary tube, placed in a bath at constant temperature and inoculated at one end with a nucleus of the solid. The crystallization is propagated through the melt, with an easily recognizable boundary between crystal and liquid, so that the distance travelled by the boundary in a given time can be read off upon a scale. The velocities of crystallization thus measured are usually expressed in millimetres per minute. In contradistinction to the velocity of crystallization of a single kind of face, the linear velocity of crystallization has no definite crystallographical meaning.

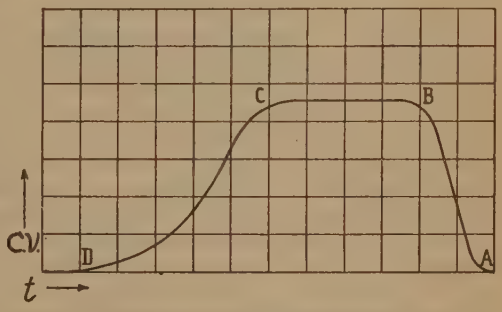

Fig. 68.—Dependence of the Crystallization Velocity upon Temperature.

The linear velocity of crystallization depends greatly on the supercooling. Small at slight supercooling, it increases as the temperature falls, reaches a maximum value, which often remains approximately constant over a considerable range of temperature, and then decreases again (see Fig. 68). In Fig. 68 the melting-point is taken as origin of the co-ordinates. Tammann [4] believes that this course only represents the true dependence of the velocity of crystallization upon temperature to a limited extent, and that it is to a large extent distorted by the conditions of the outflow of heat. He assumes that in the region of increasing velocity, just below the melting-point, the removal of heat is so inadequate that the boundary surface is heated above the temperature of the melt, whereby the velocity of crystallization is

[1] Zentralbl. f. Min., Geol. und Pal. 1917, 191.
[2] Compt. rend. **95**, 1278 (1882).
[3] "Kristallisieren und Schmelzen," p. 131 *et seq.*
[4] "Kristallisieren und Schmelzen," p. 133 *et seq.* Zeitschr. f. physik. Chemie, **23**, 326 (1897); **26**, 307 (1898); *J. Friedlaender* and *Tammann, ibid.* **24**, 152 (1897).

lessened. As the temperature falls this disturbance becomes less and less, until in the region of constant velocity of crystallization the conditions for the removal of heat are such that the temperature of the boundary surface coincides with the melting-point. On cooling still further the temperature falls also at the boundary surface below the melting-point, and now the velocity of crystallization is itself decreased since its true dependence upon temperature, right from the melting-point onwards, is really such that it declines with falling temperature.

According to experiments of Nacken [1] this view is not correct. On the one hand he was able to show that in the case of benzophenone and salol the temperature in the interior of a crystal polyhedron growing in a supercooled melt is already at a few degrees of supercooling distinctly below the temperature of melting. He further carried out experiments by allowing crystals to grow in a melt which was maintained at the temperature of the melting-point while the crystal itself was cooled ; the latter, a hemispherical piece of crystal produced by partial fusion, was attached to a metallic rod. As long as the heat produced by crystallization balanced that conducted away, the temperature of the melting-point is maintained at the surface of the crystal. The shape of the crystal piece depends only on the thermal conductivity ; it remains hemispherical (in the case of regular crystals) or ellipsoidal (in the case of other systems). If the loss of heat by conduction increases, the point may be reached at which it is greater than the heat supplied by crystallization ; this first occurs for the crystal face with the smallest velocity of crystallization. At points of the crystal surface which belong to this crystal face, the temperature sinks below the melting-point. There the velocity of crystallization, being the slowest process, determines the amount crystallizing out. A face is formed upon the rounded piece of crystal. If the loss of heat becomes greater, other faces, of greater crystallization velocity, also have an insufficient heat supply. Their temperature now also falls below the melting-point, and further crystal faces are formed. If Tammann's theory were correct, the formation of surfaces in experiments of this kind would only begin at a considerable degree of supercooling, represented approximately by the point C in Fig. 68 ; with benzophenone this would be at a supercooling of over 40°, since, while the melting-point is 47·7°, the crystallization velocity only begins to decrease sensibly below 0°. But Nacken actually found that in the case of salol and benzophenone slight supercooling of about 1·5° to 2° sufficed to generate faces, that is, to lower the temperature of the crystal surface below that of the melting-point. It was only in the case of water, which has a very great crystallization velocity (cf. Table 99, p. 327), that the supercooling could not be pushed far enough to produce faces. We must therefore conclude that the course of the curve in Fig. 68 actually represents the dependence of the crystallization velocity upon temperature ; like the velocity of formation of nuclei, the crystallization velocity also passes through a maximum as the temperature falls. The maximum is often so flat that the crystallization velocity remains constant over a considerable range of temperature. Fundamentally this course is probably to be explained in a similar manner to that of the velocity of formation of nuclei (cf. p. 320), only it does not depend upon the smaller kinetic energy of one or several molecules of the melt, but upon the kinetic energy of the molecules and crystal nuclei which impinge upon the solid crystallized face, and are there arranged in the space lattice.

In spite of this similarity between velocity of formation of nuclei and

[1] Neues Jahrb. f. Min., Geol. und Pal. **2**, 133 (1915).

velocity of crystallization, present experience favours the view that they are largely independent of one another. The following example may be given. Piperonal and apiol melt at temperatures which are not very far apart; piperonal at 37°, apiol at 30°. The velocity of crystallization of the latter substance is 7·13 mm. per minute at 0°,[1] that of the former at this temperature is also small.[2] In spite of this similar crystallization velocity, the velocity of formation of nuclei for piperonal is so great that it is hardly possible to cool it to 0° without spontaneous crystallization occurring. Apiol, on the other hand, remains liquid at 0° for many hours.[3]

Like the constants of reaction velocities, the crystallization velocities are distinguished by very great diversity. The following table, which contains a series of maximum velocities of crystallization, exemplifies these enormous differences, such as that between phosphorus (60,000 mm. per min.) and salol (1 mm. per min.).

TABLE 99

Maximum Crystallization Velocities

Substance.	Melting-point in Degrees.	Temp. of Bath in Degrees.	Vel. of Cryst., mm. per Min.	Observer and Remarks.
Phosphorus	44	+ 25	60,000	Gernez [4] (value not maximal)
Water	0	— 9·07	6,840	Walton and Judd [5] (value not maximal)
Picric acid	122	+ 85	858	Bogojawlenski [6]
Azobenzene	67·1	+ 37	600	J. Friedländer and Tammann [7]
Benzophenone (rhombic) . .	47·7	+ 20	59·5	v. Pickardt [8]
Benzophenone (monoclinic) . .	25	+ 5	2·4	Tammann [9]
Benzoin.	136	+ 80	21·4	Bogojawlenski [6]
Salol I (rhombic)	42	+ 20	3·46	Tammann [10]
Salol II.	38·8	+ 20	1·0	Tammann [10]

This table further illustrates by means of the examples of benzophenone and salol that different solid forms of the same substance have different crystallization velocities.

We cannot expect to draw conclusions as to the connexion between crystallization velocity and constitution, until the true velocity of crystallization of the various kinds of faces of a crystal has become known. In any case it seems already established that organic substances of high molecular

[1] *Tammann*, "Kristallisieren und Schmelzen," p. 146.
[2] *Tammann*, Zeitschr. f. physik. Chemie, **25**, 476 (1898).
[3] *Tammann*, Zeitschr. f. physik. Chemie, **25**, 472 and 476 (1898); also experiments by the author.
[4] *loc. cit.* p. 325.
[5] Journ. Phys. Ch. **18**, 722 (1914).
[6] Zeitschr. f. physik. Chemie, **27**, 585 (1898).
[7] *loc. cit.* p. 325.
[8] Zeitschr. f. physik. Chemie, **42**, 17, 1902.
[9] "Kristallisieren und Schmelzen," p. 146.
[10] *ibid.* p. 147.

weight and of complicated structure have a lower velocity of crystallization than the more simply constituted inorganic substances.

The Influence of Foreign Substances upon the Crystallization Velocity of Supercooled Melts

The influence on the crystallization velocity of foreign substances dissolved in the melt is very great and of a striking nature. The relations are simplest in the range of the stationary maximum velocity of crystallization; for it may be said that practically all substances lower the velocity of crystallization in that region, as appears from the experiments of v. Pickardt [1] and Padoa and Galeati.[2] There is much to support the view that this action of foreign substances depends upon their adsorption at the interface crystal-melt,[3] as was first taken into account by Marc (cf. p. 337) for crystallization from solutions. It is quite evident that an adsorption of this kind must greatly depress the velocity of crystallization. One may imagine that the adsorbed molecules of foreign substance, on the principle of displacement (cf. p. 144), diminish the number of molecules of low kinetic energy which are capable of entering into the crystal lattice; or that they occupy a portion of the boundary surface, so that the molecules which would be capable of entering it do not adhere after the first encounter. For the relative depression of the velocity of crystallization we may choose the expression $\frac{g_0 - g}{g_0}$, where g_0 is the velocity of crystallization of the pure melt, and g that of the impure.[4] The relative lowering $g = \frac{g_0 - g}{g}$ should be proportional to the amount adsorbed:

$$g = \frac{g_0 - g}{g_0} = \varkappa a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and for a the adsorption isothermal

$$a = \alpha \, . \, c^{\frac{1}{n}}$$

is supposed to hold. Hence

$$g = \frac{g_0 - g}{g_0} = \varkappa \, . \, \alpha c^{\frac{1}{n}} = k c^{\frac{1}{n}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

How far the agreement extends is shown by the following table, in which for c is put simply the concentration of the foreign substance in the melt.[5]

[1] *loc. cit.* p. 327.
[2] Gazz. chim. ital. **35, I,** 181 (1904).
[3] *Freundlich,* Zeitschr. f. physik. Chemie, **75,** 245 (1910).
[4] The expression $\frac{g_0 - g}{g_0}$ is in so far open to objection as g would acquire negative values for a high concentration of the foreign substance, which is impossible. It is therefore perhaps better to follow Marc in taking instead the expression $\log \frac{g_0}{g}$. As long as g and g_0 differ very little, $\log \frac{g_0}{g}$ passes into $\frac{g - g_0}{g}$, if the logarithm be developed into a series and the higher terms be neglected. For greater differences between g_0 and g, $\frac{g_0 - g}{g_0}$ is more easily calculated from equation (2) above than $\log \frac{g_0}{g}$.
[5] This is not strictly correct, but should be permissible here, since the amount adsorbed is certainly very small, and the equilibrium concentration therefore only very little different.

TABLE 100

Depression of the Crystallization Velocity of Benzophenone by Catechol [1]

$g_0 = 59{\cdot}5$; $k = 0{\cdot}2884$; $\frac{1}{n} = 0{\cdot}4645$; $t = 20°$

c (mol. Catechol to 100 mol. Benzophenone).	g (obs.).	g (calc.).
0·25	50·0	50·5
1	43·5	42·3
2	36·5	35·8
4	26·1	26·8
8	13·4	14·3

The value of $\frac{1}{n}$ lies between 0·2 and 0·6, as required by the adsorption isothermal.

At higher concentrations g calculated from formula (2) differs from the observed value ; the $\log_{10}g$, $\log_{10}c$ curve is not straight, but slightly concave to the $\log_{10}c$ axis, that is, the amount adsorbed decreases and approaches a saturation value, as described for adsorption in greater concentrations (cf. p. 182). This is also in full agreement with the theory of adsorption.

v. Pickardt points out a further regularity, that many substances—hardly any but aromatic ones, like catechol, benzoic acid, benzoin, naphthalene, have been examined—depress the crystallization velocity of benzophenone equally in equimolecular solution ; the constant k is uniform when c is reckoned in mols. This may also be explained by adsorption. It has already been remarked on p. 195 that in equimolecular solution related substances are often equally strongly adsorbed, and in particular it could be shown that such substances as were used by v. Pickardt—catechol, benzoic acid, salicylic acid, *m*-nitrobenzoic acid, benzoin—are adsorbed in almost equal amount by charcoal from equimolecular solutions in acetone.[2]

But it would certainly be incorrect to ascribe the influence of foreign substances upon the crystallization velocity entirely to adsorption. This

[1] From measurements by *v. Pickardt, loc. cit.* p. 327.

[2] *Freundlich* and *E. Posnjak* [Zeitschr. f. physik. Chemie, **79**, 168 (1912)].
It seems to me more probable that the depression of the crystallization velocity by foreign substances is to be explained by adsorption rather than by the following hypothesis, due to *Tammann* [Zeitschr. f. phys. Chemie, **81**, 171 (1913)]. He assumes that the foreign substances lower the melting-point at the boundary surface and thus depress the crystallization velocity. This view would explain their equal effect in equimolecular solution, but it demands an unexampled magnitude for the temperature coefficient of the crystallization velocity, for which there is no indication. A concentration of 0·05 mol of a foreign substance in 1,000 grams of benzophenone suffices to lower the crystallization velocity 30 per cent. Now the freezing-point of benzophenone falls by 9·5° for a concentration of 1 mol of foreign substance in 1,000 grams of benzophenone. The 0·05 mol would therefore cause a depression of the freezing-point of about 0·5° ; this would have to cause the 30 per cent. depression in crystallization velocity ; that is, we should have about 60 per cent. per degree. On the descending branch of the crystallization velocity-temperature curve (CD in Fig. 68) the crystallization velocity declines about 0·25 per cent. per degree. If we assumed the same temperature coefficient as for the velocity of a chemical reaction, we should still only have one of 10 per cent. per degree. See also the results of *Nacken* (p. 325).

results already from measurements by F. Dreyer,[1] who followed the influence of foreign substances upon the whole course of the crystallization velocity-temperature curve. It was found that the rising and falling branches of the curve were not equally affected by foreign substances; hence the position of the maximum could be displaced. (In v. Pickardt's experiments just discussed it was assumed that a displacement of this kind had not taken place, which was indeed shown experimentally to be correct in a few cases.) F. Dreyer found that especially on the descending branch a rise in the crystallization velocity due to foreign substances may occur, for example in melted formanilide, where it is brought about by methyl and ethyl alcohol. Tammann [2] explains this correctly as being due to these substances decreasing the viscosity and so increasing the crystallization velocity. The connexion between crystallization velocity and viscosity is particularly clear in the case of fused silicates.[3]

The crystallization velocity of supercooled melts is particularly strongly influenced by the solvation of the dissolved substances. This follows especially from measurements by Walton and Brann [4] of the velocity of crystallization of water at $-7°$. The lowering of this velocity by dissolved salts was throughout parallel to the hydration of these salts. As a measure of the hydration various characteristics were taken, especially the tendency to crystallize with water of crystallization, the amount of combined water of crystallization, and the departures from regular osmotic behaviour at high concentrations. In the case of the alkali salts we thus find the lyotropic series $Li > Na > K$; magnesium salts lower the velocity of crystallization more strongly than calcium salts, and these more strongly than those of barium. It is clear that substances which hold water molecules bound by means of their residual valencies deprive them of the opportunity of attaching themselves to the residual valencies of the ice crystals.

In these contaminated melts a further phenomenon appears, which must be discussed later in another connexion. It is observed, when a coloured foreign substance such as azo-benzene is added to benzophenone, for instance, that the very finely crystalline mass at first formed is coloured uniformly yellow. In course of time it becomes more coarsely crystalline, the coarser crystals appear pure white, and the azo-benzene finally appears at the end of the crystallization tube, collected in drops. The crystals thus expel the foreign substance between them at the interface; a phenomenon closely allied to the *reversal of adsorption* (cf. p. 453).

It has hitherto been assumed that upon solidification crystals of the pure solvent always separate. If this is not the case, and mixed crystals separate, then the velocity of crystallization is comparatively little altered, and that continuously with the composition of the melt. The crystallization velocity curve for the mixture is convex towards the axis of composition, and its course recalls the melting-point curve.[5]

If a supercooled melt is cooled rapidly to very low temperatures, so that the range of most rapid formation of nuclei is quickly passed, most

[1] Zeitschr. f. physik. Chemie, **48**, 467 (1904).
[2] See *F. Dreyer*, *ibid.* p. 480.
[3] Cf. *i.a. Kittl*, Zeitschr. f. anorg. Chemie, **77**, 335 (1912).
[4] *Walton* and *Brann*, Journ. Amer. Chem. Soc. **38**, 317 (1916); *Brann*, *ibid.* **40**, 1168 (1918).
[5] *Bogojawlenski* and *Ssacharow*, Schrift. d. Dorpat. Naturforsch. Ges. **15**, 197 (1907) cited from Chem. Zentralbl. 1907, I, 1719; *Tammann*, Zeitschr. f. physik. Chemie, **81**, 171 (1913); *Hasselblatt*, *ibid.* **83**, I (1913).

substances, as Tammann [1] has shown, solidify to *glasses*. In principle it is possible to transform every substance in this way into a glass. This is therefore not only true of solutions, like the well-known glasses consisting of silicates, phosphates, etc., but also for simple substances. In a glass we must postulate the existence of as many crystal nuclei as the temperature requires, generally indeed more, since a certain number will probably have been formed during the passage through the region of greater velocity of formation of nuclei. In a durable glass, however, the velocity of crystallization is so small that crystallization does not extend from these nuclei. If the glass is warmed to a higher temperature, at which the velocity of crystallization is maximal, crystallization proceeds further from these nuclei. *Devitrification* takes place. The time-relation of such devitrification is simply a crystallization velocity, only we have to examine from case to case what solid actually separates out.

The latent heat of fusion which is set free in the devitrification of many glasses, for example vitreous cupric metaborate and sodium metaborate, is, according to experiments by Gürtler,[2] so great that the rise in temperature caused by it produces a violent devitrification of the whole mass; the temperature rises by 200° in the process.

The Nature of the Amorphous Solid State

The state of aggregation of the glasses obtained by rapid cooling of supercooled melts is certainly to be regarded as amorphous-solid. They show all the characteristics usually ascribed to this state. This is the place to discuss them more closely.

Firstly, all properties of a glass, such as density, index of refraction, viscosity, and others, change continuously into those of the liquid. No *melting-point* can be distinguished, as is the case with a crystalline-solid substance, assuming of course that the glass during heating does not crystallize in the range of maximum crystallization velocity.

In the second place, the thermal *conductivity* of glasses has a temperature coefficient opposite in sign to that of crystalline-solid substances. The thermal conductivity of crystals increases rapidly the nearer we approach absolute zero. The thermal conductivity of glasses, on the other hand, decreases with falling temperature, apparently becoming constant in the neighbourhood of absolute zero. Eucken [3] has proved this for non-metallic crystals such as quartz and naphthalene, and for various kinds of silicate glasses. This appears to me to be a particularly important difference, which suggests that the manner in which the electrons are bound is very different in the crystalline- and amorphous-solid states. In amorphous solids the molecules, as in liquids (see p. 39), are to a great extent preserved as structural units, while in the lattice of the crystal they are replaced by atoms and atomic groups, and the whole crystal may, as it were, be regarded as a molecule.

The most useful method to distinguish the amorphous from the crystalline state depends upon the *interference of Röntgen rays* as carried out by Debye and Scherrer.[4] Its physical basis is the arrangement applied by

[1] Zeitschr. f. physik. Chemie, **25,** 468 (1898).
[2] Zeitschr. f. anorg. Chemie, **40,** 268 (1904).
[3] Ann. d. Physik (4), **34,** 185 (1911); Physik. Zeitschr. **12,** 1005 (1911).
[4] Physik. Zeitschr. **17,** 277 (1916); *Scherrer*, Nachr. d. K. Ges. d. Wiss. Göttingen, 1918, p. 98; *Scherrer* in *Zsigmondy*, "Kolloidchemie," 3rd Ed., Leipzig, 1920, p. 387 *et seq.*

W. H. and W. L. Bragg.[1] They allowed X-rays of uniform wave-length to fall upon a well-formed crystal face and determined the angle at which reflection of the X-rays by the face took place. Reflection only occurs at definite angles, at which interference of the X-rays takes place at successive planes of the crystal lattice. In most directions the rays are extinguished. They only remain in existence when the difference in the paths of rays which are reflected from successive planes of the crystal are whole multiples of the wave-length. If φ is the angle between the direction of the impinging ray and the crystal face, λ the wave-length of the ray, d the distance between parallel layers of the lattice, and n a whole number (see Fig. 69), then, as in the corresponding optical interference at a grating, we have

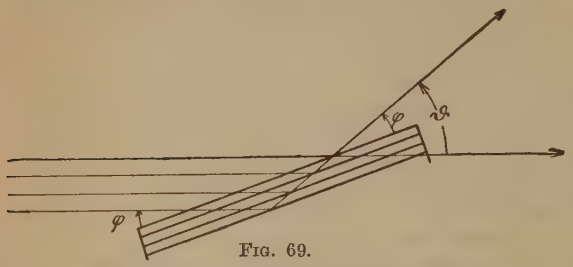

Fig. 69.

$$n\lambda = 2d \sin \varphi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Debye and Scherrer allow the monochromatic X-rays to pass through a rod compressed from the finely powdered solid, instead of upon a well-formed crystal surface. If the substance is crystalline, there will always occur among the many irregularly disposed ones some crystals which have faces in a position corresponding to the angle φ of an order n for a given λ and d. From these faces the rays will be reflected. All crystal faces of corresponding position, that is, such as with equal d and n are inclined at an equal angle φ to the incident ray, lie upon a circle around this ray; hence the reflected rays form the surface of a right circular cone of angle θ (see Fig. 69). If the rod is surrounded by a photographic film, the reflected rays record themselves as a curve (see Fig. 70).

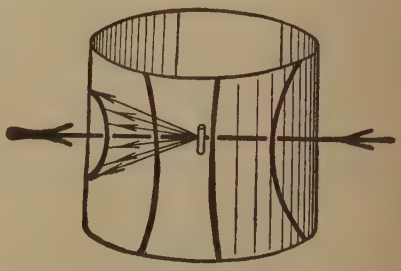
Fig. 70.

The finer the powder, or the more finely crystalline the solid, the broader are the recorded interference lines, but they lie at the same points as the fine lines of coarsely crystalline substances. With an amorphous solid, as with a liquid, no lines are obtained, but either a uniform blackening at the point where the X-rays have passed through, or quite broad interference bands. The presence or absence of the interference lines decides the question whether the substance is crystalline or amorphous.

An exact analysis of the lines of such Röntgen spectrograms permits further conclusions. We must remember in the first place that the X-rays at our disposal are not strictly monochromatic, but that we are working with rays of different wave-lengths, and have to separate the interference lines belonging to these different wave-lengths. From the position of the lines alone conclusions cannot generally be drawn concerning the *crystal*

[1] Zeitschr. f. anorg. Chemie, **90**, 153, 169, 182, 185, 219, 235, 246, 270, 277 (1914).

system. It is further necessary to determine the intensity of the lines photometrically. From this the conclusions can then be drawn as to the arrangement of the atoms in the crystal lattice. Runge,[1] and also Johnsen and Töplitz,[2] have given methods by which these calculations may best be carried out.

The breadth of the spectral lines, that is, the distribution of intensity in the single line, permits a conclusion to be drawn as to the *size of the crystal particles.* The number of lattice planes determining the reflection is characteristic for the sharpness of the spectral lines. Since the distance between the lattice planes is very small—of the order of $\frac{1}{2}\frac{1}{0}$ $\mu\mu$—the X-rays need penetrate only to a comparatively small depth, in order that a considerable number of planes may take part in the reflection ; these suffice to determine the minimum breadth. The diameter of the crystals must be as small as $100 - 10$ $\mu\mu$ for a definite broadening to take place. This is however just the size of colloid particles which are contained in sols and gels. With these, therefore, in so far as their particles are crystalline, a definite broadening takes place. It is defined by the half-value breadth B, that is, the breadth of the line at the point at which the intensity is half as large as the maximum intensity of the line in question. If we have a cubical crystal with a side of length Λ, then the relation holds

$$B = 2\sqrt{\frac{\log 2}{\pi}}\frac{\lambda}{\Lambda}\cdot\frac{1}{\cos\frac{\theta}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

an equation from which Λ, the size of the particle, can be calculated when the wave-length λ of the X-rays, d, θ, and the half-value breadth B are known.

As regards the experimental arrangement, the following points must be attended to. Pure monochromatic X-rays would be desirable, but cannot be obtained. We have not only to reckon with the various lines of the characteristic X-rays which proceed from the antikathode, but also with the " white " X-rays produced by the stopping of the kathode rays. All that can be done is to ensure that the monochromatic radiation is a sufficiently large fraction of the total. Hence not every technical X-ray tube is suitable for such exposures ; tubes must be used such as have been proposed by Rausch von Traubenberg [3] or Siegbahn.[4] The choice of the correct voltage is very important. Every characteristic radiation demands a definite minimum potential ; if it is desired to work say with the K-radiation of copper, at least 10,000 volts are required. According to Scherrer, it is advisable to make the voltage about 50 per cent. higher. For driving the tube an alternating-current transformer is, according to R. O. Herzog and W. Jancke, more convenient than an induction coil.

The rods are made about 1 centimetre long and 1 mm. thick. If the powder of the solid, the grains of which should not be larger than 10 μ in diameter, does not cohere sufficiently under pressure, it is put into a small tube of collodion, which is made by rolling up a very thin collodion film. Exact details concerning the construction of the photographic chamber are to be found in Scherrer's paper. It is important that no other secondary radiation should be generated in it besides that from the rod. The X-rays

[1] Physik. Zeitschr. **18,** 509 (1917).
[2] *Ibid.* **19,** 47 (1918).
[3] Physik. Zeitschr. **18,** 241 (1917).
[4] *Hadding,* Zeitschr. f. Physik. **3,** 369 (1920).

are therefore introduced by means of a brass tube, having a lumen of 1·5 mm. diameter, which becomes slightly larger at the end entering the chamber. Secondary rays which arise at the point of exit of the X-rays from the narrow part of the lumen are thus caught. At the place where the rays emerge there is a hole in the chamber and in the film. The rod must be carefully centred.

Experiments of this kind have shown that glasses are indeed amorphous solids. Thus Scherrer [1] found, for a variety of glass made by Goerz, a spectrum, quite free from lines, such as is also given by a liquid. Glasses, however, often show lines; although externally quite clear, they evidently contain very fine crystals, probably arising from an incipient devitrification. In Plate I reproductions are given of photographs of crystalline quartz, Fig. 71, and quartz glass, Fig. 72, from experiments by Kyropoulos,[2] which plainly show the contrast between amorphous and crystalline.

We may already point out here that jelly-like substances separated from aqueous solutions (in addition to glasses resulting from fusion) may be amorphous. In Plate I we have the X-ray spectrum of precipitated silicic acid in Fig. 73, and of a silicic acid gel in Fig. 74; in Fig. 75 that of beryllium hydroxide, precipitated from a $Be(NO_3)_2$ solution by NH_3, filtered, and cautiously dried; in Fig. 76 crystalline $Be(OH)_2$ prepared according to the method of Haber and van Oordt [3] by prolonged warming with NH_3 solution. Here again the first-named has an entirely amorphous, the latter a crystalline character.

The Velocity of Crystallization in Supersaturated Solutions

The velocity of crystallization in supersaturated solutions will here, in the first place, relate to cases in which macroscopic crystal surfaces are present in contact with the solution. We are therefore not concerned with ultramicroscopic crystals or with amorphous particles arising from the nuclei first formed; the substance present in supersaturated solution is to deposit itself exclusively upon crystal faces already present; the formation of new crystals upon fresh nuclei will be neglected.

The laws governing these phenomena have been elucidated to a great extent by Marc.[4] At one time the opinion was frequently held that the velocity of crystallization from supersaturated solution was largely similar to the velocity of dissolution of a crystal. The velocity of dissolution could be frequently referred to a diffusion velocity, as Noyes and Whitney,[5] and also Nernst [6] and Brunner [7] had shown; immediately at the surface of the crystal saturation is rapidly brought about; the dissolved substance distributes itself throughout the solution after diffusing comparatively slowly through a layer of liquid which adheres to the crystal surface in spite of strong stirring. The velocity which is measured is thus that of the diffusion through the adherent layer of liquid. It was correspondingly assumed that immediately at the crystal surface the molecules of the substance in super-

[1] *Zsigmondy*, "Kolloidchemie," 3rd Ed. Leipzig, 1920, p. 408.
[2] Zeitschr. f. anorg. allg. Chemie, **99**, 197, 249 (1917).
[3] Zeitschr. f. anorg. allg. Chemie, **38**, 377 (1904).
[4] Zeitschr. f. physik .Chemie, **61**, 385 (1908); **67**, 470 (1909); *Marc* and *Wenk*, *ibid.* **68**, 104 (1909); *Marc*, *ibid.* **73**, 685 (1910); **75**, 710 (1911); **79**, 71 (1912); Zeitschr. f. Elektrochemie, **15**, 679 (1909); **16**, 201 (1910); **17**, 134 (1911); **18**, 161 (1912); *C. L. Wagner*, *ibid.* **17**, 125, 189 (1917).
[5] Zeitschr. f. physik. Chemie, **23**, 689 (1897).
[6] *loc. cit.* p. 146.
[7] *loc. cit.* p. 146.

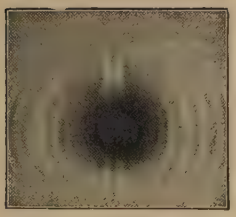

FIG. 71.—Quartz.

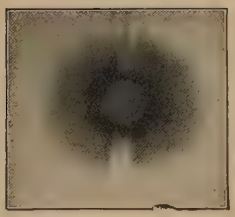

FIG. 72.—Quartz glass.

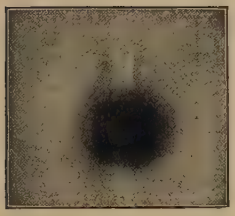

FIG. 73.—Precipitated Silicic Acid.

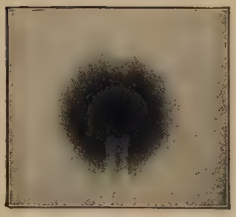

FIG. 74.—Silicic Acid Gel.

FIG. 75.
Precipitated Beryllium Hydroxide.

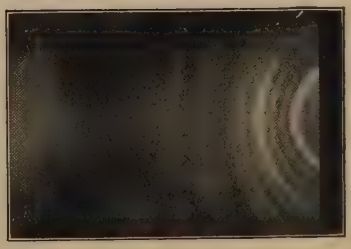

FIG. 76.
Crystalline Beryllium Hydroxide.

To face page 334.

saturated solution arrange themselves very quickly upon the surface, so that there the state of saturation was reached; a diffusion gradient was thus supposed to arise from the supersaturated solution, and the important factor would be once more the diffusion of the dissolved substance through a liquid layer adhering to the crystal surfaces.

If this view were correct, the course of the process should in each case be of the first order, and with a similar extent of the crystal surface, similar volume of liquid, and similar conditions of stirring, the velocity constants should be equal; for we have for solution

$$\frac{dx}{dt} = \mathrm{D} \cdot \omega \cdot \frac{(c_s - c)}{\mathrm{d}} = \varkappa(c_s - c), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where x is the increase in the amount in solution, t the time, D the diffusion constant, ω the surface area, c_s the concentration at saturation, c the concentration in the solution, and d the thickness of the diffusion layer. For crystallization we should have correspondingly

$$-\frac{dx}{dt} = \mathrm{D} \cdot \omega \cdot \frac{c_{ss} - c_s}{\mathrm{d}} = \varkappa(c_{ss} - c_s), \quad . \quad . \quad . \quad . \quad (2)$$

where c_{ss} is the supersaturation.

In reality this supposition was *a priori* not very probable. For since very small crystallization velocities were known for supercooled melts, there was no good reason why the velocity of crystallization should be so much greater in a solution. Marc could actually show, and this was confirmed by experiments of Le Blanc and Schmandt,[1] that at low temperatures and particularly with large surfaces and extremely powerful stirring—conditions which favour rapid diffusion—the concentration of the solute in the supersaturated solution decreases with a velocity which at high rates of stirring is independent of the latter; the constant of this velocity is quite different from that of the dissolution velocity. Such was the case, for example, for potassium sulphate, potassium dichromate, and alum. This velocity was therefore taken to be a true velocity of crystallization. In some cases it was possible to prove that the constant of dissolution velocity and that of the velocity of crystallization show considerable approximation at high temperatures; that is to say, we have finally a diffusion velocity in both cases, while at low temperatures there is a divergence.

None of these experiments was carried out under conditions enabling the crystallization velocity of a definite kind of face to be measured. It is therefore difficult to give a simple interpretation to the fact that in the experiments of Marc the time relations of the crystallization velocity are frequently of the second order. He describes as a striking phenomenon that in his experiments, in which usually a large quantity of fine crystals were whirled round in the supersaturated solution, a more rapid decrease in concentration took place in the first minutes than would have been expected from the law followed subsequently. Marc assumes that this larger decrease is due to an adsorption of the dissolved substance at the boundary of the crystals.

A connexion with adsorption is also to be expected according to the considerations put forward by Valeton [2] concerning the relation between the velocity of crystallization and the arrangement of the atoms in the space lattice of heteropolar substances. He points out the following. With the

[1] Zeitschr. f. physik. Chemie, **77**, 614 (1911).
[2] Physik. Zeitschr. **21**, 606 (1920).

cubical form of rock-salt the space lattice points are alternately occupied by Na and Cl atoms; the attraction radiating outwards to Na and Cl ions in a solution will be largely neutralized, and only when a Cl ion with sufficiently low kinetic energy strikes a Na atom in a cube face—or conversely when a Na ion strikes a Cl atom—will the ion be held fast and cause the face to grow. The crystallization velocity of the cube face is therefore very small (the crystallization velocity of a face naturally refers to the rate of growth at right-angles to this face); it is much smaller than on the octahedral faces of common salt, in which the lattice points of a face always consist exclusively of Na or Cl ions alternately; these will therefore strongly attract respectively the Cl or Na ions in the solution. Now, however, the slowly growing faces will always increase at the expense of more quickly growing neighbouring faces, a crystal is always bounded by faces of low crystallization velocity. The cube face is thus usually preferred over the octahedral face. Why under certain circumstances octahedra of common salt can nevertheless appear in certain solutions will be discussed later (p. 340).

The Influence of Foreign Substances upon the Velocity of Crystallization in Supersaturated Solutions

The pronounced difference in the effect of foreign substances on crystallization and on dissolution is important. Dissolution is as a rule hardly influenced sensibly by their presence, as indeed results from the conception

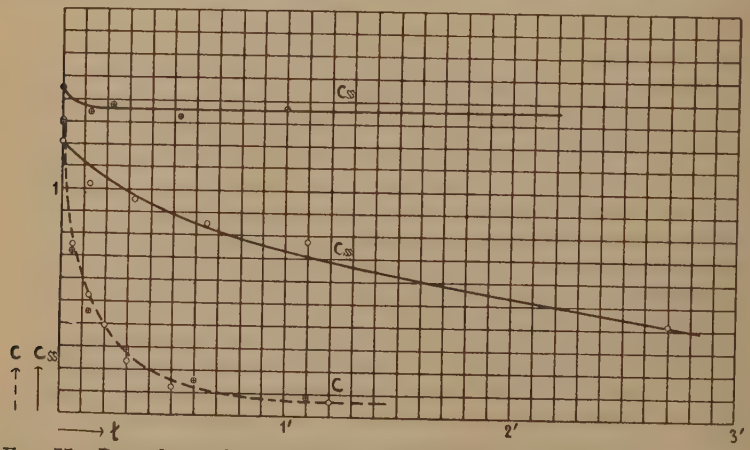

Fig. 77.—Dependence of the Velocity of Crystallization and Dissolution upon the Presence of a Foreign Substance.

of velocity of dissolution as a diffusion velocity. Thus the dissolution of potassium sulphate is not affected by the presence of 0·03 gram of quinoline yellow in 100 c.c., while crystallization is almost completely checked [1]; this appears from Fig. 77, in which are represented the decrease with time of the super- and the sub-saturation, both in the presence and in the absence of the dye. In it the full curves marked c_{ss} give the time relations of the decrease of supersaturation due to crystallization velocity; the points marked with crosses refer to the solution containing the dye. The dotted curve marked c depicts a velocity of dissolution; the points

[1] *Marc* and *Wenk*, Zeitschr. f. physik. Chemie, **68**, 112 (1910).

which relate to a solution containing the dye lie upon the same curve as those of the pure solution. The time t is given in minutes, the super- and sub-saturation in grams per 100 c.c. of solution.

It was found that only those dyes inhibit the crystallization which colour the crystals.[1] In the case of potassium sulphate these were bismarck brown, ponceau red and quinoline yellow. Methylene blue did not colour, patent blue and logwood extract only weakly ; they accordingly exerted no influence upon the velocity of crystallization, or only a very small one. Marc rightly explains this effect as depending on the adsorption of these dyes, but the influence does not depend upon the dye forming an inhibitory layer, through which the molecules of the solute must diffuse ; for then it should have a similar effect upon dissolution. In proportion to the amount adsorbed, the dye molecules displace those molecules of the solute which on account of their kinetic energy or other properties are capable of entering into the crystal lattice, and consequently the velocity of crystallization is lowered.

How the velocity of crystallization changes with the concentration of the dye is shown in Fig. 78. Here the crystallization of potassium sulphate

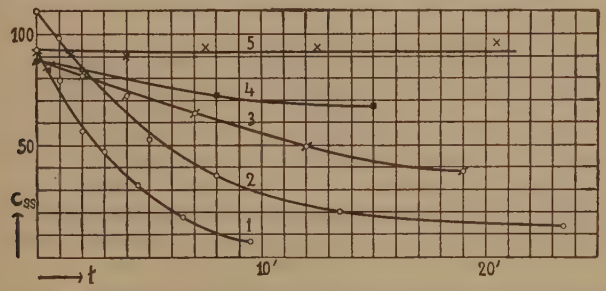

Fig. 78.—Dependence of the Crystallization Velocity upon the Concentration of a Dissolved Foreign Substance.

from supersaturated solution in presence of quinoline yellow is represented ; curve 1 relates to a pure solution, curves 2 to 5 to solutions containing dye to the amount of 0·416, 0·500, 0·583, 1·66 grams of quinoline yellow per litre. The time is again given in minutes, the supersaturation in a relative measure. A quantitative experiment is not quite easy to carry out, since—as Fig. 78 shows—at various concentrations of the dye the system tends towards a different final state. Marc [2] therefore chose for comparison the initial velocity at various dye-concentrations. As measure of the inhibitory action he chose the logarithm of the ratio $\frac{g_0}{g}$, where g_0 is the initial velocity in the pure solution, g in the one containing the dye. If this inhibition g is proportional to the amount adsorbed, then according to the adsorption isothermal (see p. 328) an equation

$$g = \log \frac{g_0}{g} = kc^{\frac{1}{n}}$$

should hold, where c denotes the concentration of the dye. The results could actually be largely represented by such a formula.[3]

[1] *Mark* and *Wenk, loc. cit.*
[2] Zeitsch. f. physik. Chemie, **73**, 708 (1910).
[3] Here also the footnote on p. 328 applies.

As has been said, in solutions containing dyes crystallization ceases, although a sensible supersaturation persists ; if the concentration of the dye is large enough, the original supersaturation may even remain unaltered. This state, which according to Marc's experiments may be preserved indefinitely, is not a state of equilibrium ; for on dissolution we arrive at the same solubility, whether we proceed from the pure crystal and the pure solution, or from crystals and solution containing the dye. In dissolution the ions of the solute, which pass into solution from the surface-layer, are generated immediately by atoms or atomic groups of the crystal, quite independently of whether the valencies extending into the liquid are occupied by dye molecules or not. This occupation of free valencies is however a strong inhibitor when ions strive to leave the solution for the space lattice. We have again the characteristic asymmetry between, on the one hand, a process, such as dissolution, in which from a directed structure with definite vectors an irregular distribution arises, depending upon the laws of probability, and, on the other hand, a process such as that of crystallization, where the molecules pass from irregular distribution into the order of the space lattice. Baur has rightly emphasized this asymmetry and has pointed out that it recurs in the synthesis of complicated organic substances from simpler ones.[1]

Crystal layers formed in a dye solution contain the dye uniformly distributed, in a kind of solid solution. It has not yet been definitely proved that the distribution is *molecularly disperse*. Not less probable is perhaps a *colloidally disperse* distribution ; the first nucleus formed in supersaturated solution is enveloped in an adsorption layer containing the dye which, like most of these layers (cf. p. 310), is a few $\mu\mu$ thick ; a fresh layer of crystals, also probably about several $\mu\mu$ in thickness, clothes nucleus and adsorption layer and adsorbs a further quantity of dye in its exterior from the solution. We should thus have a series of ultramicroscopic layers.

This is exactly the view at which Ritzel[2] arrived for so-called iron sal-ammoniac, the well-known " mixed crystals " of ferric and ammonium chlorides which are formed when NH_4Cl crystallizes from solutions containing $FeCl_3$. It appears probable from his results that we are here concerned with an adsorption. He found especially, however, that the newly separated crystals rich in $FeCl_3$ are unstable, and always change into ones containing less and less $FeCl_3$, so that in the state of equilibrium finally attained almost pure NH_4Cl crystals are in equilibrium with the solution containing $FeCl_3$. This process is of course similar to the phenomenon described above on p. 330, where the azobenzene contained as a foreign substance in the crystallized benzophenone was forced out as the crystals became coarser. In all probability the crystals containing the dye will behave similarly, and it appears possible that this is the end state towards which the false equilibria above described tend.

It may be remarked that the adsorption of foreign substances during crystallization from supersaturated solution is a very general and widespread

[1] *Baur* and *Orthner*, Zeitschr. f. physik. Chemie, **91,** 75 (1916) ; *Piazza, ibid.* **93,** 183 (1919) ; *Baur, ibid.* **93,** 240 (1919). The problem of producing living matter from non-living at present mocks any attempt at solution ; the difficulty here also consists in the necessity of passing from an arrangement of a simpler kind to one of a higher order. The molecules, atoms or atomic groups would have to pass from the irregular distribution of a gas or liquid, or from the strict order of a crystal, to the arrangement of living protoplasm, which arrangement, although it is loose, provides both for extreme segregation and for extended connexion.

[2] Chemie der Erde, **1,** 9, 270 (1914–1915).

phenomenon, and in no way rare and peculiar. In the case of dyes, $FeCl_3$ and other substances, it is disclosed by the colour; where this is not the case it is easily overlooked, if other circumstances do not bring about its recognition. Thus Reinders [1] observed the following: AgCl crystallizing from water containing NH_3 is able to take up dyes also present, such as methylene blue, and erythrosin, as is seen from the colour. Other dyes, and also substances such as gelatine and albumin, do not colour directly, but their presence in the AgCl can be recognized by the fact that its sensitivity to light increases to an extraordinary degree. In the case of gelatine an amount of 0·00001 per cent. still produced an effect.

Reinders as well as Ritzel [2] emphasize that it is not possible in many cases to demonstrate an adsorption of foreign substances by preformed crystals, while it is plainly evident when the crystal is given the opportunity of taking up the foreign substance during crystallization from supersaturated solution. One explanation might be that in the latter case a much larger surface is active—that of the crystal nuclei and of the crystal layers which are continually being formed and are only a few $\mu\mu$ thick. Here it is possibly of importance that we are dealing with an order of magnitude of crystals in which the interfacial tension is of importance in connexion with their form (cf. p. 156). On the other hand, one might also imagine, in connexion with the experiments of Barger described on p. 189, that at first an amorphous, strongly adsorbing form of the solid separates, which changes extremely quickly into the crystalline form, without the adsorbed substance having time to leave the surface in accordance with its lessened capacity for being adsorbed.

It is very probable that the cases already touched upon on p. 190, in which crystalline substances also take up iodine, often with a blue colour (cholic acid, flavone, etc.), are likewise "solid solutions" of the kind just described. In these cases also the substance is not taken up by formed crystals, but during crystallization from a solution, and it may be unhesitatingly assumed that at first an amorphous separation takes place; with cholic acid, for example, amorphous granules are often found lying alongside the fine crystals. Barger and Miss Field [3] have measured the adsorption isothermal of iodine both for crystalline and for amorphous cholic acid. The stronger adsorption with the amorphous adsorbent is very marked. Whether the curve for the crystalline adsorbent really corresponds to states of equilibrium is a question I should like to leave open for the present. It is quite possible that it is here a question of crystallization velocity, and thus of the time which the adsorbed substance has at its disposal to leave the boundary surface, at which it is perhaps really much more weakly adsorbed. The departures from the usual adsorption isothermal, which Barger and Miss Field observed for the adsorption of I_2 by crystalline cholic acid, and Reinders [4] for the adsorption of dyes by crystalline AgCl, may be connected with this.

The presence of foreign substances often markedly affects the *shape of the crystals*; usually a one-sided development appears to be favoured by the foreign substance as opposed to a more usual all-round development. Consider, for instance, the peculiar dendritic crystals of AgCl which arise in the presence of methylene blue (Fig. 79B on Plate II) compared with the simple

[1] Zeitschr. f. physik. Chemie, **77**, 213, 677 (1911).
[2] *loc. cit.* p. 338.
[3] Journ. Chem. Soc. **101**, 1394 (1912).
[4] Zeitschr. f. physik. Chemie, **77**, 683 *et seq.* (1911).

regular structure of the pure crystals in 79A (Reinders).[1] This is probably to be explained by the different crystal faces adsorbing with different intensities, or the velocity of crystallization, which varies according to the direction, being lowered to a different extent by the foreign substance, or perhaps both circumstances may come into play. It is perhaps not unjustifiable to conclude, in the many cases in which any kind of foreign substance influences crystallization, that an adsorption of the foreign substance takes place, even if this adsorption be so small that it cannot be demonstrated.

The substances of high molecular weight hitherto discussed are not the only ones which influence the velocity of crystallization in solution. Marc and Wenk [2] found, for example, that the crystallization velocity of potassium sulphate was also changed by such substances as KCl, KNO_3, K_2CO_3; it is lessened by some, and increased to double by others, in particular by KCl. The crystals which separated from solutions containing foreign substances were only slightly different from pure crystals, so long as it was a question of the small crystals which separated from strongly stirred solutions. But the differences were plain, when they separated from unstirred solutions. In this connexion the reader may be reminded of the well-known fact that common salt crystallizes from solutions containing urea in octahedra instead of cubes.[3]

In order to explain these processes more exactly, we shall have to know more about the influence of foreign substances upon the crystallization velocity of the various kinds of faces. The standpoint of Valeton previously discussed (p. 335) already allows of the following conclusions. The crystal faces of heteropolar substances which grow slowly in pure solution ought to adsorb feebly, those which grow quickly ought to adsorb strongly; for in the slowly growing faces the residual valencies are largely saturated, in the quickly growing this is not the case. In solutions containing a dye the probability is therefore great that the crystallization velocity of strongly adsorbing faces which grow quickly in pure solutions will be so greatly reduced as to be as small as, or smaller than, that of the faces which grow slowly in pure solution. The appearance of faces improbable in pure solutions becomes increasingly probable. Thus we can explain the fact that in solutions of common salt containing urea octahedra appear instead of cubes, whereby it is naturally assumed that an adsorption of urea takes place at the octahedral faces; a similar explanation is available for the above-mentioned dendritic form of crystals in solutions containing dyes, if the crystallization velocity of the various faces is greatly altered from its value in pure solution.

The phenomena just described are of very general importance. The necessity of so carefully purifying with charcoal those solutions from which it is desired to obtain crystals, depends in preparative chemistry upon the fact that possible impurities of high molecular weight lower the velocity of crystallization, and can even prevent crystallization completely when the supersaturation is appreciable. The very different habit of naturally occurring crystals is caused by crystallization from solutions containing foreign matter. The same is true of the structures containing crystals in

[1] Zeitschr. f. physik. Chemie, **77**, 680–681 (1911).
[2] *loc. cit.* p. 334.
[3] See on this point e.g. *Ritzel*, Zeitschr. f. Kristallogr. **49**, 152 (1911).

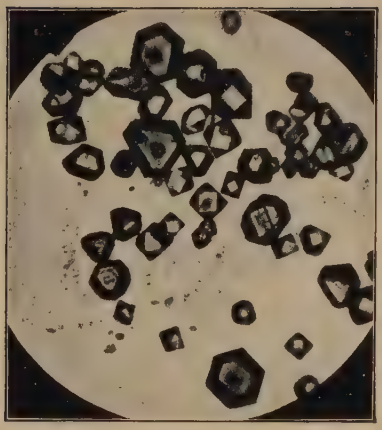

FIG. 79A.

FIG. 79B.

To face page 340.]

living organisms, such as gall-stones, urinary calculi, pearls, etc.[1] In these, however, the content of colloidally disperse substances, such as proteins, and the like, is so great, that in their formation we are dealing with a coagulation from a colloidal solution rather than a crystallization (cf. p. 597). But for the crystal form and the extremely finely crystalline structure the strong check upon the crystallization velocity due to the colloids is of decisive effect.

C. BROWNIAN MOLECULAR MOVEMENT

Brownian molecular movement is a phenomenon of fundamental importance for all colloidally disperse systems. Almost all its laws have been discovered by the ordinary microscope with coarse emulsions and suspensions. They could therefore have been discovered long before the invention of the ultra-microscope, had it not needed preoccupation with colloidal solutions and the beautiful and vivid nature of the Brownian movement under the ultra-microscope to emphasize the importance of this phenomenon. It is therefore expedient to discuss its properties, before colloidally disperse substances themselves are considered.

The Fundamental Properties of Brownian Molecular Movement

In the year 1827 the botanist R. Brown[2] described the unceasing, irregular, dancing motion which very fine granules suspended in a liquid exhibit under the microscope. He first observed it with pollen grains, but found that all available solids showed the same phenomenon when sufficiently finely powdered. For many years no further importance was attached to it, evidently because it was supposed to be due to chance motion caused by external vibration or convection currents.

Chr. Wiener[3] was the first to emphasize that one could not alter this motion in any way by excluding external influences. He therefore arrived at the view that Brownian movement is a phenomenon such as would be demanded by the kinetic theory of heat; the irregular impacts of the surrounding liquid molecules against the suspended particles he considered to be the cause of the motion. This view was more firmly established by the extensive experiments of Gouy.[4] He worked, for example, in a cellar, in which a mercury surface exhibited no vibrations; in order to keep the temperature as constant as possible he placed the preparation in a trough filled with water, into which the objective of the microscope dipped; he illuminated with light of various colours and various intensity, without influencing the nature or magnitude of the Brownian movement in any way.

Cantoni[5] was able to prove with a preparation protected from evaporation that no change in the movement took place in the course of a year. The idea was occasionally put forward[6] that the movement might be similar

[1] See e.g. *Schade*, Münch. Med. Wochenschr. 1909, **1**; Kolloidchem. Beihefte, **1**, 375 (1910). Also one of the oldest monographs on colloid chemistry, *Ord's* "The Influence of Colloids upon Crystalline Form and Cohesion" (London, 1879), relates to these phenomena, without however contributing to their explanation.

[2] Phil. Mag. 1826, **4**, 101; 1829, **6**, 161; Edin. New. Phil. Journ. 1828, **5**, 358; 1830, **8**, 41.

[3] Pogg. Ann. **118**, 79 (1863).

[4] Journ. d. Phys. **7**, 561 (1888); Compt. rend. **109**, 102 (1889).

[5] Nuov. Ciment. **27**, 156 (1867).

[6] *Maltézos*, Ann. de chim. et de phys. (7), **1**, 559 (1894).

to that of camphor particles on a liquid surface (cf. p. 70), and thus be due to local differences in velocity of dissolution, etc. The impossibility of this explanation follows particularly from an observation by Hartley [1]: fine gas bubbles in the liquid enclosed in minerals showed the Brownian movement just as vividly as it is observed in other cases; in the course of thousands of years local irregularities of that kind must have had time to disappear.

In contradiction to the kinetic theory of the phenomenon appeared to be the statement that the addition of electrolytes causes the disappearance of Brownian motion [2]; for there was no obvious reason why the impact of liquid molecules should be affected in this manner by the presence of salt molecules. Svedberg,[3] however, showed that this influence upon the Brownian movement is only apparent. In the presence of the electrolyte, the suspended particles are enabled to cohere; this cohesion will be dealt with later in connexion with the theory of coagulation (see p. 416). Hence from small particles larger ones are formed, so that the limit is soon reached at which no further motion can be observed and the particles settle down. If Svedberg took sufficiently dilute suspensions, so that as few collisions as possible took place between the particles, he found that the Brownian movement of the single unchanged particles was in no way altered by the electrolyte.

An objection raised by Nägeli [4] was perhaps a further check to the development of the molecular-kinetic theory of the phenomenon. He put forward the following considerations: In his opinion a single molecular impact was too weak to produce a visible motion of the particle. But the molecular impacts cannot be summated; they take place irregularly from all sides, and should therefore cancel one another, and the suspended particle should remain at rest. However, this conception only holds, as v. Smoluchowski [5] pointed out, when the time during which the particle is observed is extremely long. In a game of chance one may lose or win a stake many times over in a given moderately long time. Gains and losses will only cancel when the game is extended over a very long time. The theory of probability gives the probable number of molecular impacts upon the particle in a given direction as so great that in the time we have for observation we may not regard ourselves as observers over a very long period, but as over a definite, moderately long time. During this the impacts in a given direction may so preponderate that we are able to recognize a motion of the particle.[6]

[1] Proc. Roy. Soc. **26,** 150 (1877). Cf. also *Gouy, loc. cit.*

[2] *Jevons,* Proc. Manch. Phil. Soc. **9,** 78 (1869), and *Gouy, loc. cit.*

[3] Nov. act. reg. soc. scient. Upsal. (4), **2,** No. 1, pp. 146–155. Statements have nevertheless been made [e.g. by *Henri,* Compt. rend. **147,** 62 (1908), about particles of a rubber emulsion] that even before union of the particles, salts lower the velocity of the *Brownian* movement; here we are probably concerned with an increase of size, not directly visible, and due to an adsorption envelope.

[4] Sitzungsber. d. Münch. Akad. d. Wiss. **9,** 389 (1879).

[5] Ann. d. Physik (4), **21,** 762 *et seq.* (1906).

[6] The argument may be illustrated as follows. Imagine a large and heavy block of wood floating on a lake, and around it on all sides persons armed with revolvers continually firing at it, absolutely at random. The total impulse given to the block by the bullets will never balance exactly at any time, but on the other hand, it will rarely be so one-sided as to give the block a sufficient impulse to move it, say, several times its own diameter in any given direction. For each degree of one-sidedness of impulse there will be a certain displacement of the block; the degrees of one-sidedness will fall off rapidly in frequency the greater they become, according to an ordinary probability curve. We shall therefore have to watch the game for a certain length of time on the average in order to see a certain displacement take place, and this time

The theory of Brownian motion from the molecular-kinetic point of view was developed by Einstein [1] and v. Smoluchowski.[2] The latter gave as the fundamental idea of his treatment that the mean kinetic energy of a particle which is moved by the blows of the surrounding molecules of liquid is, in a stationary condition, equal to that of the surrounding molecules; that is to say, it behaves as if it were a molecule of a dissolved substance. Einstein tacitly based his work upon the same view, by postulating that particles in Brownian movement exert the same osmotic pressure upon a wall impermeable to them as the same number of molecules would exert. This view has been confirmed quantitatively down to its ultimate consequences.

The Validity of the Hypsometric Formula in an Emulsion

This may already be demonstrated in the case of a phenomenon for which it is not necessary to follow the Brownian movement in detail. Just as the density of a gas and the concentration of a solution decrease with increase in height, so the concentration of an emulsion or suspension must also decrease at higher levels, since the particles behave as if they were molecules of a dissolved substance with very high molecular weight.

For the decrease in density of a gas with increasing height the hypsometric formula

$$h = \frac{RT}{gM} \log \frac{p_0}{p}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

holds. Here h is the height, p_0 the pressure at the surface of the earth, p at the height h, g the acceleration due to gravity, M the molecular weight, R and T have the usual meaning. It results from this formula that for a given decrease in pressure the height is the smaller the greater the molecular weight. Since one may place the molecular weight of the particles of an emulsion at about 100,000,000 times that of oxygen, then (at 0°) the height at which the concentration of the emulsion falls off to one half only amounts to 50 μ, since in an oxygen atmosphere we must (at 0°) rise 5,000 metres for the density to be halved.

Perrin [3] succeeded in proving that aqueous emulsions of gamboge and mastic show this phenomenon in a pronounced manner. A gamboge emulsion is produced simply by grinding gamboge with water; a milky emulsion of mastic is produced by pouring an alcoholic solution of mastic into a considerable excess of water. Perrin first showed that the number of particles (see Fig. 80) decreases logarithmically with the height, as required by the hypsometric formula, and further, that a state of equilibrium is established, for if a uniform distribution of the particles is produced artificially, the original state of regular decrease with the height is soon restored.

In order to be able to test whether the gas laws or van 't Hoff's laws for dilute solution really hold quantitatively for these emulsions, as is implied

will increase rapidly with the displacement it is desired to observe. If the minimum observable displacement is so great that the probability of its occurrence is very small, we shall practically never see any displacement of the block. [*Trans.*]

[1] Ann. d. Physik (4), **17**, 549 (1905); **19**, 371 (1906); Zeitschr. f. Elektrochem. **13**, 41 (1907); **14**, 235 (1908).

[2] Ann. d. Physik (4), **21**, 756 (1906).

[3] Compt. rend. **146**, 967 (1908); **147**, 530, 594 (1908); **152**, 1380 (1911); Ann. de chim. et de phys. (8), **18**, 5 (1909). Cf. also *Perrin-Lottermoser*, "Die Atome," Dresden u. Leipzig, 1914. Further experiments by *Iljin*, Zeitschr. f. physik. Chemie, **87**, 366 (1914).

by the application of formula (1) the latter must first be transformed somewhat. The osmotic pressure, which takes the place of the gas pressure, is proportional to the number of particles present in unit volume, therefore

$$P_0 = kn_0$$

and

$$P = kn.$$

Further, the molecular weight M is equal to Avogadro's number N, the number of molecules in 1 mol (gram molecular weight), multiplied by the weight of a single particle of the emulsion. The particles are strictly spherical and have a radius r, their density is ϱ; the buoyancy, and hence the density ϱ_l of the liquid, must be taken into account. We therefore get in place of formula (1) the equation

$$h = \frac{RT}{gN\frac{4}{3}\pi r^3(\varrho - \varrho_l)} \log \frac{n_0}{n}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The equation presupposes that all particles have the same radius r. Since this was not so in the emulsion at the outset, a uniform emulsion had to be prepared artificially. Perrin achieved this by fractional centrifuging. If an emulsion with particles heavier than the liquid be centrifuged, the largest particles are thrown down first. The finest remain suspended in the liquid for the longest time. Particles below a certain size can thus be removed. Now it is possible to re-emulsify the precipitated particles by treatment with water, and hence a middle fraction of particles of uniform size can be separated, which just remain suspended at a certain velocity of centrifuging, while all particles above a certain size are centrifuged off.

Fig. 80.

The numbers n and n_0 are determined by limiting the field of view of a microscope by means of a diaphragm to such an extent that the number of particles can be quickly counted. The mean values of a large number of estimates were taken as the values of n and n_0, h is given by the vertical displacement of the microscope. The radius r was measured by Perrin in several ways:

1. Upon drying, the particles frequently arrange themselves in chains, so that the radius can be calculated from the length of a chain and the number of particles in it.

2. In weakly acid solution the particles completely adhere to the glass walls of the trough, without coalescing to larger drops, so that they can be counted there. If the content of the suspension is determined analytically, one can find from the total weight of the particles and their number the weight of a single particle; a knowledge of the density then gives the radius.

3. The radius of the particles may be determined from their rate of falling by means of Stokes' formula

$$u = \frac{2}{9} \frac{r^2(\varrho - \varrho_l)g}{\eta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Here u is the velocity of the falling particle, r its radius, ϱ its density, ϱ_l and η are respectively the density and viscosity of the liquid. In order to determine u, the emulsion was poured in a state of uniform distribution into a tall vessel, in which it stood higher than corresponded to the stationary distribution of the particles; in falling the particles showed a sharp line of demarcation from the supernatant clear liquid, so that the velocity with which this line moved downwards could be conveniently determined. The density of the particles could be determined by known methods.

We can therefore calculate N from equation (2), since R is known. Perrin found in his best series of experiments with gamboge particles of radius 0·367 μ and density 1·195 at 20° $N = 68{\cdot}2 \times 10^{22}$. The most probable value from other measurements is 61×10^{22}. Perrin's value is therefore only a few per cent. higher.

Similar correct values of N were obtained with an emulsion containing 12 per cent. of glycerine, which was therefore very viscous,[1] and also at temperatures of −9° (under-cooled aqueous emulsion) and of 58°.[2]

There can thus be no doubt that equation (2) holds. The particles of very dilute emulsion distribute themselves under the influence of gravity in the same numerical fashion as do the molecules of a gas or of a dissolved substance. The Brownian movement therefore entirely corresponds to the molecular movement required by the kinetic theory; on account of this movement the particles exert an osmotic pressure, for which van't Hoff's laws $PV = RT$ hold. It is thus in every respect justifiable to treat the emulsified particles as very large molecules.

The Displacement as a Measure of the Brownian Movement

The Brownian movement can still be recognized with particles of about 4 μ diameter. With these it shows itself as an irregular trembling motion, apparently about a fixed position. With smaller particles we have an equally irregular dancing with considerable displacement in space. Attempts to record the position of a particle during a given period of time give a zig-zag path, such as is represented in Fig. 81. Exner [3] hoped to measure the velocities of the particles of a gamboge emulsion by determining the time taken to traverse this path. He found in the case of particles of about 0·4 μ diameter a velocity of about 0·0004 cm. per sec. According to the kinetic theory the kinetic energy of the particle should equal that of the impinging molecules of the liquid. The velocity c of the particle and that of the liquid molecule c_0 should therefore be inversely proportional to the square roots of the molecular weights, hence

$$c = c_0 \sqrt{\frac{M_0}{M}}.$$

For a probable value of the velocity of the water molecules $c_0 = 150$ metres per second and a molecular weight of the particles of $2{\cdot}4 \times 10^{10}$ we get $c = 0{\cdot}4$ cm. per sec., a much larger value, therefore, than that found by Exner.

This is not in contradiction to the kinetic theory, for v. Smoluchowski [4] rightly points out that the velocity cannot be determined by Exner's

[1] *Perrin* and *Bjerrum*, Compt. rend. **152**, 1569 (1911).
[2] *Perrin-Lottermoser*, "Die Atome," p. 96.
[3] Ann. d. Physik (4), **2**, 843 (1900).
[4] Ann. d. Physik (4), **21**, 764 (1906).

method. The motion of the particle is so irregular, that in much shorter intervals of time than Exner took into account a considerable change of direction takes place; the shorter the periods of time during which the observation is made, the more complicated is the zig-zag path, the longer the distance traversed in the total time, and the greater the velocity. Even the shortest periods of time which can be realized in the experiment are too long to allow of a measurement of the true velocity.

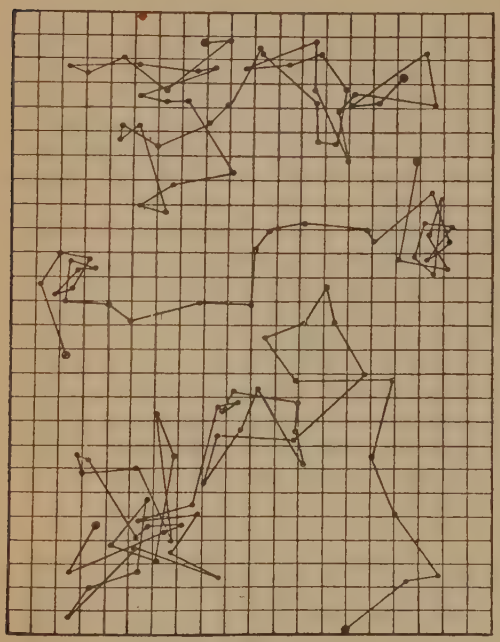

Fig. 81.

Einstein and v. Smoluchowski therefore take another magnitude to characterize the Brownian movement, viz. the *displacement* of the particle during a certain interval of time. This is simply the straight line connecting the initial and the final position of the particle, as observed over a certain time interval. Since under the normal experimental conditions with a microscope the processes are followed in a horizontal plane, it is the projection of the true motion upon this plane, the *horizontal displacement*, which is found. Usually only the horizontal displacement in one direction is taken into account; hence along one axis of co-ordinates.

If the kinetic theory holds, then from the initial position of a particle as zero point in a horizontal plane a displacement in the positive sense in a certain direction x is as probable as one in a negative sense. The smallest displacements are the most probable, greater ones become more and more improbable, *i.e.* Gauss' curve of errors, as represented in Fig. 82, holds for these displacements. This curve gives the horizontal displacements as abscissæ, and the probabilities, that for a horizontal displacement a value between x and $(x + dx)$ is reached as ordinates. This probability is given by the equation [1]

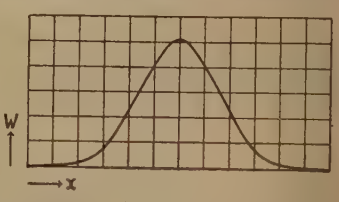

Fig. 82.—Gauss' Curve of Error.

$$W = \frac{1}{\sqrt{2\pi\xi^2}} e^{-\frac{x^2}{2\xi^2}} dx. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here ξ^2 is the mean of the squares of the mean horizontal displacement.

[1] For its deduction see *de Haas-Lorentz*, "Die *Brownsche* Bewegung," Braunschweig, 1913, p. 13 *et seq.*; further *Timerding*, "Die Analyse des Zufalls," Braunschweig, 1915, p. 91 *et seq.*

As v. Smoluchowski remarks, the displacement of particles in the Brownian movement may be illustrated very clearly by means of Galton's board. This (see Fig. 83) is a gently inclined board, in which a large number of nails have been driven in alternating rows. A ball, the diameter of which is so chosen that it can just slip between two nails, will, when allowed to roll down from a point in the upper edge, experience displacements which, depending entirely upon chance, correspond completely to those occurring in Brownian movement. Indeed, in its behaviour such a ball represents perfectly the particles of an emulsion which, falling under the influence of gravity, undergo oscillations induced by Brownian movement. If from the middle of the upper edge a large number of balls are allowed to roll down, instead of a single one, and if they are collected below in compartments, the resultant distribution (see Fig. 83) corresponds to the Gaussian curve of error; in the middle, corresponding to small displacements, we have the largest number of balls; their number falls off rapidly on either side, while fewer and fewer balls experience the larger displacements.

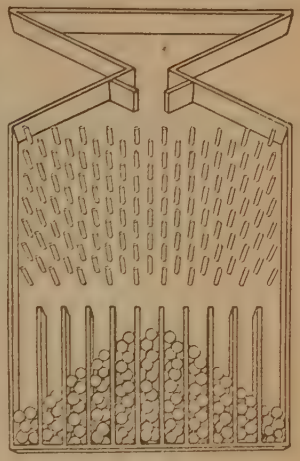

Fig. 83.

If N displacements have been observed, the number ΔN which corresponds to a given magnitude of displacement is given by

$$\Delta N = N \int_{x_1}^{x_2} \frac{1}{\sqrt{2\pi\xi^2}} e^{-\frac{x^2}{2\xi^2}} dx. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Table 101

Validity of Gaussian Curve of Errors for Horizontal Displacements

Horizontal Displacement x (in μ), the magnitude of which lies between	N (obs.).	N (calc.).
0 and 1·7	48	44
1·7 „ 3·4	38	40
3·4 „ 5·1	36	35
5·1 „ 6·8	29	28
6·8 „ 8·5	16	21
8·5 „ 10·2	15	15
10·2 „ 11·9	8	10
11·9 „ 13·6	7	5
13·6 „ 15·3	4	4
15·3 „ 17·0	4	2

We must therefore multiply the number N by the probability, and integrate between the limits within which the displacement is to lie. Table 101, taken from measurements by Perrin and Chaudesaigues,[1] shows that the

[1] *Perrin-Lottermoser*, "Die Atome," p. 109.

theory holds. The horizontal displacements of particles of a gamboge emulsion ($r = 0{\cdot}212\ \mu$) were observed; the time interval was 30 secs.

The Relation between the Displacement and the Diffusion of the Particles

The mean displacement ξ is closely connected with the diffusion of the emulsified particles, as may be seen from the following treatment by Einstein,[1] which, although not rigorous, is nevertheless clear. Let diffusion take place in a horizontal tube of unit cross section in the direction of x.

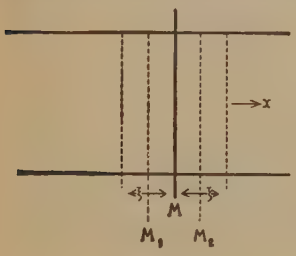

Fig. 84.

The passage of particles across the plane M (see Fig. 84) will be considered. In the time t only those particles can pass through which are separated from M by a distance smaller than the mean displacement ξ. If c_1 is the concentration of the particles in the plane M_1, then $\frac{1}{2}\xi c_1$ particles can pass through M; the factor $\frac{1}{2}$ indicates that, since the displacement in a negative sense is equally likely, only half the particles may be assumed to be moving in a positive direction. At the other side of M only those particles displaced in the negative sense will move through M. Their number is similarly $\frac{1}{2}\xi c_2$, where c_2 is the concentration in the plane M_2. In the direction of diffusion, therefore, $\frac{1}{2}\xi(c_1 - c_2)$ particles pass through M in the time t. Now let ξ be so small that we may put

$$\frac{c_2 - c_1}{\xi} = \frac{dc}{dx}.$$

Hence, since

$$c_1 - c_2 = -\xi\frac{dc}{dx}$$

the number of particles passing through M is

$$-\frac{1}{2}\xi^2\frac{dc}{dx}.$$

In unit time this number is

$$-\frac{1}{2}\frac{\xi^2}{t}\frac{dc}{dx}.$$

Now the number of particles passing through unit cross section in unit time is simply the coefficient of diffusion D, if the gradient of concentration $\frac{dc}{dx} = 1$. Hence

$$\mathrm{D} = \frac{1}{2}\frac{\xi^2}{t}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Since at constant temperature D is constant for a given emulsion

$$\frac{\xi^2}{t} = \text{Const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

[1] Zeitschr. f. Elektrochemie, **14**, 235 (1908).

The square of the mean displacement is proportional to the time of observation. This relation has been fully confirmed.

If the value $\xi^2 = 2Dt$ be introduced into formula (1), p. 346, for the probability W, we get

$$W = \frac{1}{2\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} dx, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

a formula which is frequently used.

The relation between Brownian movement and diffusion may also be explained by means of Galton's board (Fig. 83).

If the balls at the upper edge of the board are arranged according to a given law of density, and are allowed to roll down, the gradual advance of the balls corresponds to the diffusion of particles into a liquid column. It clearly results from this that diffusion is a simple consequence of Brownian movement, as soon as the distribution does not correspond to a state of equilibrium. We must not therefore assume an osmotic pressure to be acting in addition to the Brownian movement; the osmotic pressure is, as it were, a macroscopic expression of the same cause that is observed microscopically as Brownian movement. It is the same antithesis as was noticed on p. 234 in explaining adsorption; the osmotic pressure is a thermodynamic magnitude, the displacement due to Brownian movement a molecular-kinetic one.

By aid of the osmotic pressure, Einstein[1] further deduces a relation between the coefficient of diffusion, the size of the particles, and the viscosity of the liquid (see again Fig. 84). If the velocity of a diffusing particle be u, then we have for u

$$u = \frac{k}{R}$$

where k is the force exerted on the particle, and R the frictional resistance experienced by it. Now let the concentration of the particles in front of the section M, through which they are to pass, be c mol. Since in 1 mol N particles are present, c mols contain cN particles; consider that these particles together are subject to the force K. Then

$$u = \frac{1}{cN} \frac{K}{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The force acting in diffusion is the gradient of osmotic pressure P. Hence

$$K = -\frac{dP}{dx},$$

and since

$$P = RTc,$$

it follows that

$$K = -RT\frac{dc}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By substituting (5) in (4) we get

$$uc = -\frac{RT}{NR} \frac{dc}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

[1] *loc. cit.* p. 348.

According to an equation given by Kirchhoff the frictional resistance experienced by a sphere of radius r in a liquid of viscosity η is given by

$$R = 6\pi\eta r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which may be introduced into (6)

$$uc = -\frac{RT}{6\pi N\eta r}\frac{dc}{dx}.$$

Now uc is simply the amount passing through unit section in unit time; and since for unit gradient of concentration this is equal to the diffusion coefficient D, we have

$$D = \frac{RT}{6\pi N\eta r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If we put the expression for D in (8) equal to that in (1), it follows that

$$\frac{\xi^2}{t} = \frac{RT}{3\pi N\eta r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This is the important equation, first given by Einstein,[1] which connects the displacement in the Brownian movement with the time of observation, the radius of the particles, and the viscosity of the liquid. It was confirmed semi-quantitatively by Svedberg,[2] and quantitatively by Perrin [3] with the gamboge and mastic emulsions, used also in his other experiments, by Seddig [4] with aqueous suspensions of cinnabar, and by Seelis [5] with cinnabar suspensions in aqueous glycerine solutions. As a proof the value of N may again be given which was deduced from the displacement of gamboge particles ($r = 0{\cdot}367\ \mu$, $t = 20°$); it was $68{\cdot}8 \times 10^{22}$.[6]

With gamboge particles in a glycerine solution, which was 125 times more viscous than the pure aqueous emulsion, the correct value $N = 64 \times 10^{22}$ was again obtained.[7]

Instead of measuring the displacements in a horizontal plane, this may also be done in a vertical one. For example, the fall of very small drops of mercury in water is followed, the drops being so small that they do not fall quite vertically, but on account of molecular motion continually experience lateral displacements. After Zangger and Böhi,[8] and later v. Ettenreich,[9] had carried out measurements of this kind, very careful experiments on

[1] By means of a different argument *v. Smoluchowski* arrived at a formula which only differs from *Einstein's* by a numerical factor. Experiment has confirmed *Einstein's* formula.

[2] Nov. act. reg. scient. Upsala (4), **2**, No. 1 (1907); Zeitschr. f. Elektrochemie, **12**, 853, 909 (1906).

[3] *Perrin-Lottermoser*, "Die Atome," p. 101 *et seq.*, especially p. 114. *Chaudesaigues*, Compt. rend. **147**, 1044 (1908); *Perrin* and *Dabrowski*, Compt. rend. **149**, 477 (1909).

[4] Zeitschr. f. anorg. Chemie, **73**, 360 (1912).

[5] Zeitschr. f. physik. Chemie, **86**, 682 (1914).

[6] According to *Costantin* [Ann. de Physique (9), **3**, 113 *et seq.* (1915)] this value of *Perrin's* is too great, for the following reason. The *Einstein* formula assumes the validity of *Stokes'* law; but this is not strictly true in the neighbourhood of a solid wall. The troughs used by *Perrin* were so narrow that this influence of the wall made itself felt in the gamboge emulsions.

[7] *Perrin* and *Bjerrum*, *loc. cit.* p. 345; Shaxby [Proc. Roy. Soc., A, **104**, 655 (1923)] has determined Avogadro's number from observations on bacteria.

[8] *Zangger*, Kolloidzeitschr. **9**, 216 (1911); *Böhi*, "Untersuchungen zur Kapillar- und Diffusionsanalyse." Diss., Zürich, 1911.

[9] Sitzungsber. d. Wien. Akad. d. Wiss. **121**, IIa, 1163 (1912).

submicronic mercury particles were undertaken by Nordlund,[1] in which the motions of the particles were registered by an automatic photographic camera. He found a value for N of $59{\cdot}1 \times 10^{22}$, which lies nearer to the probably correct value of 61×10^{22} than the majority of the values determined from molecular motion.

Equation (9) shows the great intensification of Brownian movement by decrease in the size of the particles; to this attention has frequently been drawn, and also to the fact that its increase at higher temperatures is especially due to the decrease in viscosity resulting from the rise of temperature. Particular material constants do not occur in the formula, in accordance with the experimental fact that the movement is independent of the chemical nature of the particles, of their density, electrical charge, etc.

The Brownian Rotatory Movement

Einstein further came to the conclusion that in addition to the translatory Brownian movement, the emulsified particles must have a rotatory motion. For this he deduced, by reasoning similar to that employed for equation (9) (p. 350), the relationship

$$\frac{A^2}{t} = \frac{RT}{4\pi N \eta r^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where A is one-third of the square of the mean angle of rotation in the time t.

This equation also was tested and confirmed by Perrin.[2] The particles of ordinary gamboge and mastic emulsions rotate too quickly and hence do not allow of measurement. He therefore produced particles of about 50 μ diameter by slow action of water upon an alcoholic solution of mastic. Since these are so heavy that they remain lying on the bottom of the vessel, he suspended them by increasing the density of the water by the addition of urea. The rotatory motion of the particles could be recognized by the fact that they frequently had small enclosures which could be used as reference marks. Thus for particles of radius $6{\cdot}5$ μ a value of $A = 14{\cdot}5^{\circ}$ per minute was found, from which a value of $N = 65 \times 10^{22}$ was calculated according to equation (1).

Equation (1) differs in an important respect from equation (9), p. 350, in that the parameter A which determines the motion is connected with the third power of the radius, while ξ is only connected with its first power. Hence as the size of the particles decreases, the rotatory motion increases very much more rapidly than the translatory.

The Brownian Movement of Non-spherical Particles

Equation (9), p. 350, may be expressed generally if the frictional resistance R be left as such. We have then for the mean square of the change of

[1] Zeitschr. f. phys. Chemie, **87,** 40 (1914). Further also *R. Fürth* [Ann. d. Physik (4), **53,** 177 (1918), and **59,** 409 (1919)]. He uses instead of the displacement the time taken by a particle to travel between two reference marks, and discusses the formulæ which hold for this quantity. It then results that the motion in a horizontal plane must be sharply distinguished from that in a vertical one; arithmetical approximations which for motion in a horizontal plane still lead to a formula agreeing with experiment, produce incorrect values for motion in a vertical plane.

[2] *Perrin-Lottermoser,* "Die Atome," p. 115 *et seq.* *Perrin,* Compt. rend. **149,** 549 (1909).

a parameter ξ in the time t

$$\frac{\xi^2}{t} = \frac{2RT}{NR} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This equation applies also to the displacement of non-spherical particles. For ellipsoidal ones R may again be expressed by an equation

$$R = 6\pi\eta r,$$

only r is now a complicated function of the length of the axes of the ellipsoid.

If the a axis of the ellipsoid is always the one parallel to the direction of motion whose velocity u is being observed, we have, if a, b, and c are the axes of the ellipsoid,

$$r = \frac{8}{3}\frac{abc}{X_0 + a_0a^2}$$

in which $X_0 + a_0a^2$ is a complicated function of the lengths of the axes. If the motion takes place in the direction of the longitudinal axis, if therefore $a > b$ and $b = c$, then

$$X_0 + a_0a^2 = -\frac{ab^2}{a^2 - b^2}\left[2a + \frac{2a^2 - b^2}{\sqrt{a^2 - b^2}}\log\frac{a - \sqrt{a^2 - b^2}}{a + \sqrt{a^2 - b^2}}\right].$$

If conversely it takes place in the direction of a transverse axis, so that $a < b$ and $a = c$, then

$$X_0 + a_0a^2 = \frac{a^2b}{b^2 - a^2}\left[b + \frac{3a^2 - 2b^2}{\sqrt{b^2 - a^2}}\log\frac{b - \sqrt{b^2 - a^2}}{b + \sqrt{b^2 - a^2}}\right].$$

For motion in the direction of the longitudinal axis the frictional resistance is therefore smaller, and the mobility greater, than for motion in a direction at right-angles.

Przibram,[1] who drew these conclusions, was able to confirm them completely, using chains of killed *Bacillus subtilis*; he found a correct value for N.

Magnitude and Rate of Variations in the Number of Particles in Brownian Movement

In an emulsion in which the particles have attained an equilibrium in accordance with the hypsometric formula, we will consider a definite volume, delimited geometrically, not mechanically. If the number of particles contained in it is determined at definite intervals of time, this number will be found to change continuously as a result of the Brownian molecular movement; the number of particles undergoes lasting variations. Thus Svedberg [2] found for a colloidal gold solution, to which the same considerations apply as to the emulsions hitherto considered, the numbers given in Table 102, when the sol was illuminated at regular short intervals of time ($\frac{1}{3}\frac{1}{9}$ minute) for a very short period (0·12 sec.).

[1] Sitzungsber. d. Wien. Akad. d. Wiss. **121**, IIa, 2339 (1912).

[2] "Die Existenz der Moleküle," Leipzig, 1912, p. 148. Zeitschr. f. physik. Chemie, **77**, 147 (1911).

TABLE 102

Variations in a Colloidal Gold Solution

1	2	0	0	0	2	0	0	1	3	2	4	1	2	3	1	0	2	1	1	1	1	3	1	1	2
5	1	1	1	0	2	3	3	1	3	3	3	2	2	1	1	1	2	2	4	2	2	1	2	2	6
1	2	2	1	4	2	3	4	5	2	4	1	1	4	1	3	1	1	4	2	3	1	0	0	1	0
0	4	2	1	1	2	3	1	2	3	2	0	1	1	1	1	0	0	0	1	1	1	2	1	1	0
0	1	3	2	0	0	0	0	0	1	0	0	1	1	0	0	0	1	0	0	0	2	3	2	2	1
0	0	2	1	1	0	0	0	0	2	0	1	0	0	1	3	3	3	1	2	2	0	0	0	2	3
1	2	2	1	0	2	4	0	1	1	1	0	2	1	2	2	2	1	1	2	2	3	1	0	0	0
1	1	0	3	3	1	1	1	0	2	1	0	1	1	0	0	1	0	1	0	3	0	1	1	3	1
2	1	2	1	0	1	0	1	2	1	1	1	1	2	1	1	1	0	0	0	3	2	2	1	0	1
2	3	0	2	0	1	2	1	2	1	3	2	1	1	1	0	1	1	0	0	2	3	3	1	2	2
4	2	1	1	0	0	0	1	2	0	3	0	1	0	1	0	0	2	2	1	7	3	4	4	1	0
1	0	1	0	0	2	1	1	2	2	1	1	4	4	4	4	2	1	2	1	1	4	4	0	1	3
2	1	2	3	3	1	4	3	1	3	0	1	1	2	2	2	1	2	3	3	1	0	1	2	1	1
1	1	2	2	2	4	1	2	2	3	1	1	1	3	3	2	2	1	3	2	1	1	0	0	0	0
4	1	0	4	3	2	0	1	2	1	2	0	0	1	1	3	2	2	2	3	1	2	0	0	2	5
3	2	1	2	0	3	3	2	3	3	1	1	1	1	0	0	2	1	0	0	2	2	0	1	3	0
1	1	3	2	1	1	3	1	2	0	0	1	0	1	3	1	4	3	2	2	1	1	2	2	1	1
2	2	3	2	3	4	4	2	2	2	3	0	3	2	1	4	2	1	5	3	2	2	0	0	2	0
2	1	4	2	1	2	3	2	3	2	0	4	3	1	1	2	3	1	2		0	3	3	1	4	2
2	3	4	5	2	1	3	4	1	1	0	4	1	2	3	2	2	2	2	0	2	2	1			

Two properties must here be distinguished: in the first place the probable magnitude of the departure of the number of particles from the number which would be present with uniform distribution, that is, the relative frequency of the number differing from the average number; this is the magnitude of variation. Secondly, the change with time of these variations, i.e. the probability of a given number recurring within a given period of time: the *variability rate.*

The *variability number* may be considered first. If n is the number of particles present at any given time, ν the average number present, then the probability that the number n is present in volume V is

$$W(n) = \frac{e^{-\nu}\nu^{n}}{n!} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and if we call

$$\delta = \frac{n - \nu}{\nu}$$

the *degree of departure*, then the mean degree of departure is

$$\sqrt{\overline{\delta^2}} = \frac{1}{\sqrt{\nu}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

v. Smoluchowski[1] first obtained this relationship. R. Lorenz and Eitel[2] have shown in detail how it may be deduced.

In Table 103 the directly observed frequencies $\Delta . k$ of Svedberg's numbers given in Table 102 are set out, as obtained by multiplying W (n) by the total number k. The calculated values agree well with the observed ones. $\sqrt{\overline{\delta^2}}$ further worked out at 0·803, while 0·798 was observed. ν was equal to 1·55. The rapid decrease in the frequency of numbers which deviate greatly from the average value is therefore again very pronounced.

[1] *Boltzmann*-Festschrift, 1904, p. 626. Bull. Acad. Cracov. 1907, p. 1057. Ann. d. Physik (4), **25**, 205 (1908); Physik. Zeitschr. **13**, 1069 (1912); **16**, 321 (1915); **17**, 557 (1916).

[2] Zeitschr. f. physik. Chemie, **87**, 293, 434 (1914).

TABLE 103 [1]

Variability Numbers

n.	Δk (obs.).	Δk (calc.).
0	112	109·9
1	168	170·4
2	130	132·0
3	69	68·2
4	32	26·4
5	5	8·2
6	1	2·1
7	1	0·5

When Svedberg and his collaborators [2] first tested these relationships upon various sols and emulsions, formula 1 did not appear to hold; such deviations occurred as to suggest that van't Hoff's laws ceased to hold even at comparatively low concentrations. This was all the more surprising since the same sols, at the same concentrations, appeared, according to their behaviour in the sedimentation equilibrium, to obey van't Hoff's laws. Westgren [3] succeeded in clearing up this discrepancy. The counting of particles in an optically delimited volume by means of the ultramicroscope may easily be affected by errors. In the field of observation of the slit ultramicroscope (see p. 388) there is a sharply defined image of the slit, and on either side a region which is more feebly illuminated, since the rays are incompletely united and light is reflected from the illuminated particles. If comparatively many strongly illuminated particles are in the image proper, the more feebly illuminated ones in the neighbouring regions will be neglected. They will, however, be included, if there are only few particles in the strongly illuminated field. The single values therefore cluster too closely around a mean value, which leads to apparent departures from van't Hoff's laws. This source of error is avoided if the slit is not made too narrow, and the brightness of the light diffracted from the particles is diminished by light-filters.

Questions of fundamental importance are raised in the discussion of the rate of variability. v. Smoluchowski [4] has the merit for having developed the argument and made the necessary calculations, thereby solving a problem beset with formidable difficulties.

Since the rate of change in the number of particles of a volume V, conceived to be delimited, depends upon the rate at which the particles diffuse into and out of this volume in consequence of the Brownian movement, it is at once evident that the same circumstances influence the rate of change as also affect the diffusion constant, viz. the viscosity of the liquid and the radius of the particles. Indeed, the argument may be developed in such a manner that the diffusion constant can be calculated from such observations of variations. Secondly, the *average time of recurrence* is particularly impor-

[1] *v. Smoluchowski*, Physik. Zeitschr. **17**, 561 (1916).

[2] *Svedberg*, Die Existenz der Moleküle, p. 96; Zeitschr. f. physik. Chemie, **73**, 547 (1910); *Svedberg* and *Katsuji Inouye*, *ibid.* **77**, 145 (1911); *Westgren*, *ibid.* **83**, 151 (1913).

[3] Arkiv f. Matem., Astron. och Fys. **11**, No. 8 (1916).

[4] Sitzungsber. d. Wien. Akad. d. Wiss. **123**, 2381 (1915); **124**, 263, 339 (1915); Physik. Zeitschr. **16**, 321 (1915); **17**, 557 (1916).

tant, that is, the average time which elapses before a number of particles n, once present, occurs again.

First we consider the relation to diffusion. v. Smoluchowski arrived at an equation

$$\overline{\Delta}^2 = 2\nu\mathrm{P} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Here $\overline{\Delta}^2$ is the mean square of the change in the number of particles that occurs within a time t; ν has the previous meaning; P the probability that a particle, initially present anywhere in volume V, crosses the boundary in the time t, introduces the connection with diffusion. P depends upon the shape of the delimited space under consideration. In the most trustworthy experiments, which Westgren [1] carried out with gold sols in order to test this relationship, the delimited illuminated space was a cylinder, which was bounded above and below by glass surfaces, so that the particles could only enter and leave at the cylindrical surface. For this case v. Smoluchowski has calculated P, for which purpose he employs development in series or the general equation

$$\mathrm{P} = e^{-2\alpha}[\mathrm{L}_0(2\alpha) + \mathrm{L}_1(2\alpha)]. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Here L_0 and L_1 are Bessel functions with imaginary arguments which may be taken from tables. α is a function which contains the radius a of the cylinder, the diffusion constant D and the time of observation t.

$$\alpha = \frac{a^2}{4\mathrm{D}t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

From the observed variations, therefore, the mean square of the change $\overline{\Delta}^2$ and ν can be determined, and P calculated from equation (3). For P the argument α may be deduced from (4), and from (5) the diffusion constant D. From these one can finally calculate, by means of Einstein's formula (8), p. 350, Avogadro's number N. Westgren found for gold particles of radius 63·5 $\mu\mu$ $\mathrm{N} = 60{\cdot}9 \times 10^{22}$ (at room temperature) in good agreement with the value which is assumed to be most probable.[2]

The *average time of recurrence* Θ_n is, as has been said, the interval of time which elapses between the cessation of a state with n particles to its next recurrence. In addition we must distinguish the *average duration of existence* T_n, the length of time during which on the average a state with n particles persists; the series of figures in Table 102 show that a number n may persist over several successive periods of time. Calculation gives

$$\Theta_n = \frac{\tau}{1 - \mathrm{W}_n(o)} \cdot \frac{1 - \mathrm{W}(n)}{\mathrm{W}(n)} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and

$$\mathrm{T}_n = \frac{\tau}{1 - \mathrm{W}_n(o)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Here τ is the time interval separating successive observations (in Table 102 $\frac{1}{3}\frac{1}{5}$ minute). $\mathrm{W}(n)$ is the probability introduced in equation (1) for the appearance of the state with n particles. $\mathrm{W}_n(o)$ is the probability that this state n is preserved, that is, that the number of particles in the volume

[1] Ark. f. Matem. Astron. och Fys. **13**, No. 14 (1918).

[2] According to *P. C. van Arkel* [Physik. Zeitschr. **21**, 465 (1920)] equation (3) does not give such good results for the experiments of *Svedberg*, reproduced in Table 102, as *v. Smoluchowski* imagines.

neither increases nor decreases. Table 104 shows how far the agreement goes for Svedberg's figures given in Table 102 ; in the neighbourhood of the average number ν (= 1·55) the duration of existence T_n is greatest, the time of recurrence Θ_n smallest. The latter increases greatly as the number n departs widely from the number ν.

TABLE 104 [1]

Average Time of Recurrence Θ_n and Average Duration of Existence T_n

n.	Θ_n (obs.) in Seconds.	Θ_n (calc.)	T_n (obs.) in Seconds.	T_n (calc.)
0	9·35	8·52	2·57	2·26
1	4·81	4·86	2·31	2·38
2	6·32	6·23	2·11	2·12
3	12·1	12·4	1·92	1·89
4	28·6	32·1	1·89	1·72

If values of n are considered which greatly depart from the average value, then both the probability of their occurrence and the duration of their persistence is small, that is, $W(n)$ and $W_n(o)$ are very small and may be neglected as compared with 1. If then the value of W_n from (1) is substituted in (6) we get

$$\Theta_n = \tau \frac{e^{\nu} \cdot n\,!}{\nu^n} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

It follows, for instance, from this equation that the number 7, observed only once by Svedberg, recurs on the average after 28 minutes ; the number 17 would, however, occur only once in 50,000 years, an indication how vanishingly small the chance is for the appearance of such a wide departure from the average.

Formulæ (6) to (8) contain the time interval τ separating the observations, and one cannot pass from *intermittent* to *continuous* observation simply by making τ zero. This is a point of fundamental importance not only for the rate of variation, but also for the whole previous discussion of Brownian movement. The treatment always presupposes that during the time of observation the motion of the particles may already be regarded as irregularly zig-zag. It may never be so brief that in it the motion of the particle is already rectilinear. For the deduction of formula (1) (p. 346) presupposes that we are dealing with a true displacement, *i.e.* with the line joining two points of a path which has been traversed by irregular, zig-zag steps. According to Einstein [2] it is quite possible to form an estimate of the lower limit of this time interval. It must correspond in order of magnitude to the time within which the particle would lose its velocity by friction in the liquid, if it were not kept moving by continual fresh molecular impulses. The force which drives the particle forward on account of its initial velocity u_0, viz.

$$m \cdot \frac{du}{dt},$$

[1] *v. Smoluchowski*, Physik. Zeitschr. **17**, 566 (1916).

[2] Ann. d. Physik (4), **19**, 340 (1906). See also *Perrin* in *Eucken's* "Theorie der Strahlung und der Quanten," Abhandl. d. deutsch. Bunsen-Ges. 1914, p. 157.

must be equal and opposite to the force of friction $6\pi\eta r u$, hence

$$-m\frac{du}{dt} = 6\pi\eta r u,$$

where m is the mass of the particle, r its radius, and η once more the viscosity of the medium. Integration gives

$$u = u_0 e^{-\frac{6\pi\eta r t}{m}}.$$

The particle has practically lost its velocity when $u : u_0$ as $1 : e^{10}$, when therefore

$$\frac{6\pi\eta r t}{m} = 10$$

and

$$t = \frac{10m}{6\pi\eta r}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

For particles such as were considered on p. 345, with a radius $r = 0{\cdot}367\ \mu$, we get a time of about $\frac{1}{1000000}$ sec. We see that the times of observation employed greatly exceed the permissible limit, but that, on the other hand, we may not proceed to make t zero.

But, as v. Smoluchowski [1] shows, formulæ for the average time of recurrence and the average persistence can nevertheless be deduced also for infinitely small times, that is, for continuous observation. For this it is only necessary, in considering the entrance and exit of the particles into and out of the volume V, that we do not reckon with a diffusion velocity, but with the rectilinear real velocity c which they possess in accordance with the kinetic theory of gases ; such a velocity was taken into account above (p. 345), and may be calculated from the kinetic gas equation

$$\mathrm{c} = \sqrt{\frac{3\mathrm{RT}}{\mathrm{N}m}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

In the very short times, which are smaller than the time t limited by equation (9), we are not concerned with the irregular zig-zag Brownian movement, but with particles which cross the boundaries of the volume in rectilinear paths like gas molecules. v. Smoluchowski then finds for the time $\tau = o$ a limiting value for P

$$\lim_{t=o} \mathrm{P} = \frac{\omega}{\mathrm{V}} \cdot \frac{\mathrm{c}t}{\sqrt{6\pi}},$$

where ω is the boundary surface of the volume V. When he applies this to the deduction of the formulæ for the average duration of existence and average time of recurrence he obtains the equations

$$\mathrm{t}_n = \frac{\mathrm{V}}{\omega} \frac{\sqrt{6\pi}}{\mathrm{c}(n+\nu)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and

$$\theta_n = \mathrm{t}_n \cdot \frac{1 - \mathrm{W}(n)}{\mathrm{W}(n)} = \frac{\mathrm{V}}{\omega} \cdot \frac{\sqrt{6\pi}}{\mathrm{c}(n+\nu)} \cdot \frac{1 - \mathrm{W}(n)}{\mathrm{W}(n)} \quad . \quad . \quad . \quad (12)$$

If we calculate with the aid of these formulæ the example adduced above on p. 356, we obtain for $n = 17$ an average time of recurrence of $\theta_n = 161$

[1] *loc. cit.* p. 354.

days, but a duration of existence of only 9×10^{-7} secs.; hence even with continuous observation one would not succeed in observing the recurrence of such an unusual departure from the average value. If n and ν are large numbers, some approximations may be introduced, which lead to the formula

$$\theta_n = \frac{V \cdot \pi}{\omega \cdot c} e^{\nu \frac{\delta^2}{2}} \sqrt{\frac{3}{\nu}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where

$$\delta = \frac{n - \nu}{\nu}$$

is again the degree of deviation and c is calculated from equation (10).

In this formula appears very clearly what was of course also contained in the earlier ones for intermittent observation, that the spatial extent of the volume under observation is of great influence upon the length of the time of recurrence; this influence of the volume is contained both in the ratio $\frac{V}{\omega}$, and in the magnitude of the number ν. Table 105 gives an example of such a dependence, calculated according to formula (13). It deals with spherical spaces of radius a in an emulsion of spherical gamboge particles of radius $r = 0{\cdot}367\ \mu$, as referred to in connexion with Perrin's experiments on p. 345. Suppose in a space of radius 0·0001 cm. there are 10,000 particles; the time of recurrence of the number n is calculated which is 10 per cent. greater. As we see, in small spaces such a variation is frequent; indeed, Table 102 shows that with smaller numbers of particles even very much greater variations follow one another rapidly. With increasing volumes times of recurrence are soon reached which render the occurrence of a variation of 10 per cent. exceedingly improbable. In the region of microscopic spaces these variations are indeed no longer frequent, but they still occur within finite times of observation, so that in principle it should be possible to observe them.

TABLE 105

Dependence of the Times of Recurrence (with Continuous Observation) upon the Size of the Observation Space

a (in cm.).	θ_n (in seconds).
$1 \cdot 10^{-5}$	$8{\cdot}6 \cdot 10^{-6}$
$2{\cdot}5 \cdot 10^{-5}$	$1{\cdot}1 \cdot 10^{-5}$
$5{\cdot}0 \cdot 10^{-5}$	$1{\cdot}9 \cdot 10^{-3}$
$7{\cdot}5 \cdot 10^{-5}$	4370 = 73 Min.
$10 \cdot 10^{-5}$	$1{\cdot}3 \cdot 10^{16}$
$100 \cdot 10^{-5}$	$10^{10^{4\cdot34}}$

These phenomena concerning the variation of the number of particles in a given space throw a new light upon the Second Law of thermodynamics,[1] and completely confirm Boltzmann's view, that this law is one true at the

[1] *v. Smoluchowski, loc. cit.* p. 354; further, Bull. d. l'Acad. d. Scienc. d. Cracov. 1915, p. 164; cf. also *Svedberg*, Zeitschr. f. physik. Chemie, **59**, 451 (1907).

limit, when the behaviour not of single molecules but of a large number is considered. The most probable course of a process is that accompanied by a decrease of free energy and an increase of entropy. With a small number of molecules in a small space, processes which are in contradiction to the Second Law can continually occur. We need only consider the oscillations of emulsified particles in a field in a vertical plane. Particles will enter the field which, coming from below, perform their motion against gravity. They therefore do work against gravity at the cost of the impacts of liquid molecules, which are thereby cooled; the diffuse heat of the surroundings is thus transformed into work in contradiction to the Second Law. It would indeed not be possible to employ this work in a machine, since it occurs quite by chance; moreover, one cannot imagine a mechanical arrangement which would always retain a particle just raised, and use it as a source of energy.

It is also naturally in contradiction with the Second Law, when, as in Svedberg's experiments given in Table 102, 7 particles collect, of themselves, in a given space in which equilibrium had been attained by diffusion and which should, under these conditions, contain 1·55 particles. When we consider single molecules in small spaces diffusion is not strictly irreversible. The appearance of particles in numbers deviating greatly from the average equilibrium number is, as explained on p. 356, improbable, and becomes more improbable the greater the deviation; in other words, the time of recurrence is great—for large deviations, indeed, great beyond all conception. v. Smoluchowski[1] summarizes this behaviour in the sentence: A process appears reversible or irreversible according as the time of recurrence of the initial state is short or long in comparison with the period of observation.

It appears to me that the time of recurrence is very important for biological phenomena.[2] In the case of living processes we are, it is true, never dealing with true equilibria, but always with processes running down in course of time; but in limiting cases (e.g. in a dormant germ) these proceed so slowly that the stationary state there existing may be compared with a state of equilibrium. The concentrations of dissolved substances or of colloid particles in such a structure will therefore be subject to variations. Now in the case of cells or autonomous compartments of cells we are always dealing with spaces of microscopic size, in which fairly large variations may occur in periods of recurrence (months, years, or decades) which are quite imaginable and of not too short a duration. It appears to me possible that *Mutation*, which is of such decisive importance for the development of the species, must be referred to such large variations; it might occur, say, when fertilization coincides with an unusually large variation in the germ-cell of sufficiently long duration. I do not consider it to be impossible that we may some day be able to calculate the appearance of mutation upon the basis of the law of probability, provided we know the mechanism of its appearance; it is more probable that we shall succeed in deducing the probable mechanism from the percentage of mutations occurring.

It would however be necessary to assume that substances of essential importance to life occur in minute concentrations in single cells, in amounts that can be counted, so to speak, for only then would the variations be great enough. I regard it as entirely probable that such amounts of matter are active in biological processes. It may be recalled what excessively small amounts of odoriferous substances must be taken into account in order to explain the attraction of the males by the females in certain insects; or the mixtures of substances which are transferred by the semen as inheritance.

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[1] Physik. Zeitschr. **17**, 568 (1916).

[2] *Freundlich*, "Die Naturwissenschaften," **7**, 832 (1919).

COLLOIDALLY DISPERSE SYSTEMS

In the following pages the properties and behaviour of colloidally disperse systems will be dealt with. Many coarsely disperse structures may often be readily discussed in connexion with colloidally disperse systems, which have usually been more closely investigated. The division of the subject into pairs of material states, according to the scheme on p. 3, would be the clearest form of arrangement. In practice, however, this is not convenient, since one would have first to discuss less known structures such as mist, smoke, and foam, although much would have to be assumed which was first discovered in the case of colloidal solutions. The latter, including both sols and gels, will therefore be considered first, especially as they have been far more extensively investigated. Mists, smoke, foam, and disperse structures with solid dispersion media will then follow.

A. COLLOIDAL SOLUTIONS: SOLS AND GELS

I. SOLS

Colloidal solutions in the widest sense contain a liquid as dispersion medium and a liquid or solid phase in colloidally disperse distribution as disperse phase.[1] This definition is undisputed as far as it refers to colloidal solutions in the narrower sense, i.e. to *sols*. This is not true, however, for *gels*. Formerly it was generally believed that in their case the dispersion medium was solid amorphous, the disperse phase liquid. In some cases, however, it has become practically certain that the dispersion medium is also liquid. This will be discussed later (see p. 659). In any case sols and gels are so closely related that they must necessarily be considered in direct connexion with one another.

In the limiting cases sols can be distinguished from true solutions without any difficulty. The characteristic taken advantage of by Graham,[2] that many membranes, such as parchment, collodion, and others, form semi-permeable walls, through which colloidally disperse particles, in contrast to truly dissolved ones, cannot pass, may always be used. In many cases the ultramicroscope allows the particles to be directly recognized. It is sometimes disputed (see p. 452) how far relations, such as those comprised in the theories of chemical equilibrium and dissociation, which hold for dilute true solutions, may be applied without change to colloidal solutions. But that a completely continuous transition from the true to the colloidal solution exists has already been emphasized (cf. p. 2), and will be considered more in detail later (p. 532).

Much more difficult is the question of a satisfactory division of the sols themselves. Every observer is forcibly struck with the difference between say an arsenious trisulphide sol and a gelatine solution. The As_2S_3 sol, which even with a very low As_2S_3 content is externally readily distinguishable from water on account of its deep yellow colour, is hardly different from water as regards density, surface tension, and especially viscosity. It is fairly unstable; quite small amounts of electrolyte—even salts such as NaCl, KCl, and the like, are active at concentrations of 0·1 mol and less—suffice to separate the As_2S_3 in flakes from the liquid. The gelatine solution, on the other hand, which is externally little different from water, proves even with a low gelatine content to be much more viscous; density and surface tension are also distinctly changed, and the stability, particularly towards inorganic electrolytes with univalent ions, is much greater;

[1] A certain ambiguity arises in the term "disperse phase" as soon as we pass on to sols, the particles of which differ little in size from molecules, and which might therefore be regarded as monophasic solutions. Concerning this see, for example, *Dabrowski* [Bull. Acad. d. Scienc. d. Crac. 1912, p. 486]. *Büchner* [Kolloidzeitschr. **14**, 2 (1914)] and others would prefer to regard also polyphasic structures as homogeneous from this point of view.

[2] *loc. cit.* p. 1.

if it is desired to produce a separation of the disperse phase by means of salts such as NaCl, KCl, and the like, very concentrated solutions must be employed.

It must be recognized that all sorts of transitions occur between the two classes, and even that sols of one and the same substance may belong to one group or the other according to the method of preparation or to the experimental conditions. But in the majority of cases the two original types are well defined.

Wo. Ostwald [1] proposed to distinguish two groups of sols, *suspension colloids*, or *suspensoids*, and *emulsion colloids* or *emulsoids* ; suspensoids with a solid, emulsoids with a liquid disperse phase. These two groups have frequently been treated as equivalent to the above-mentioned two natural classes, represented by the As_2S_3 and the gelatine sols. This was not Ostwald's intention. He believed, it is true, and with some justification, that many sols, which belong to the gelatine group, have a viscous liquid disperse phase, and hence must be classed as emulsions, but was quite clearly of opinion that, for example, emulsions of oil drops and mercury sols, the particles of which are certainly liquid, must on account of their properties be assigned to the class of As_2S_3 sols. Since therefore the state of aggregation of the disperse phase is unquestionably not decisive for the striking natural differences of the sols, we have the choice either to use the expressions suspensoid and emulsoid not in the original sense, but to transfer them, as is frequently done, to the two natural classes, or to retain them in their original sense and then distinguish the two natural classes by other terms. The latter appears to me to be the better course.

The division into *irreversible* and *reversible*, or into *irresoluble* and *resoluble*,[2] does not appear to me to be convincing. A sol belongs to the irresoluble (irreversible) class when its disperse phase, dried up under certain conditions, e.g. by evaporation at ordinary temperatures over sulphuric acid, is not again brought into colloidal solution by contact with the dispersion medium, while it belongs to the resoluble (reversible) class when this can be done. That this classification does not coincide with the two natural classes above-mentioned might be allowed to pass, if it were otherwise very striking. But it appears to me to be very arbitrary to select as distinguishing feature so narrow a point of distinction as the behaviour of a sol when dried under certain conditions of experiment. For this distinction must be taken in a very narrow sense, as otherwise it is not sufficient. Small differences in the content of foreign matter can make a great deal of difference whether the dried disperse phase redissolves or not ; it also depends upon the rate of evaporation and upon other matters.[3] If one only departs a little further from the prescribed distinction, one and the same sol may appear resoluble or irresoluble according to the treatment. The flakes of a V_2O_5 sol coagulated with KCl can easily be peptized (that is, brought again into colloidal solution by washing with water) ; those coagulated with $AlCl_3$, however, cannot.

More suitable is the distinction between *lyophobic* and *lyophilic*, or, since we are usually dealing with aqueous colloidal solutions, between hydrophobic and hydrophilic sols.[4] Substances such as gelatine, albumin,

[1] *loc. cit.* p. 2 ; further Kolloidzeitschr. **11**, 230 (1912).

[2] *Zsigmondy*, "Kolloidchemie," Leipzig, 1912, p. 3 ; further Kolloidzeitschr. **13**, 109 *et seq.* (1913).

[3] See *Wo. Ostwald*, Kolloidzeitschr. **11**, 236 (1912).

[4] *Perrin*, Journ. d. Chim. phys. **3**, 84 (1905).

etc., have a strong affinity for water. They "imbibe" it, become hydrated. It is therefore probable that the disperse phase of their sols consists of an amorphous-solid aqueous solution of these substances; they are certainly also hydrophilic in the sense of the wetting experiments on p. 160. Conversely, the particles in metal, sulphide, and other sols are little hydrated, and are also hydrophobic in the sense of the wetting experiments. But this division still retains something artificial. The sols of the hydroxides of iron, aluminium, and other substances correspond, in their conditions of stability, their ready coagulability by small concentrations of electrolyte, completely to the class of As_2S_3 sols. Their particles are, however, certainly rich in water and probably also hydrophilic in the sense of the wetting experiments referred to above. One is compelled to call these sols hydrophobic, which nomenclature receives some justification from the fact that they form in many respects, for example viscosity, a transition between hydrophobic and hydrophilic sols.

A really natural classification would be *electrocratic* sols for the As_2S_3 class, and *non-electrocratic* for gelatine, protein, etc. For it is undoubtedly a common property of all sols which belong to the sulphide class, that they are coagulated by electrolytes in small concentrations, and that this is closely connected with the electrical properties of the colloid particles, while with the sols of the gelatine class the electrical properties of the particles play a very subordinate part, and the stability towards electrolytes is striking.

It would, however, be difficult to apply this division to non-aqueous sols, since at present so little is known about their stability. Otherwise the only objection to the new terminology would be that it is new, and that colloid chemistry is already overloaded with technical terms. I shall therefore generally employ in the following pages the expressions lyophobic and lyophilic, hydrophobic and hydrophilic sol, and thus distinguish the two above-mentioned natural classes. If the expressions suspensoid and emulsoid are used it will be in the true sense as referring to the state of aggregation of the disperse phases, and not synonymous with lyophobic and lyophilic.

To the lyophobic sols belong the sols of many elements, such as selenium, tellurium, the metals, many oxides and hydroxides, sulphides and many others. This is only true, as will be shown later (p. 594), when they do not contain so-called protective colloids in considerable quantities. To the lyophilic sols belong silicic acid, stannic acid, the proteins, gelatine, starch, and many others. In the case of many sols, such as that of sulphur, it depends upon the method of preparation whether the sol is hydrophobic rather than hydrophilic. The most completely investigated sulphur sols appear to be more hydrophilic and will be considered later (p. 615).

It is always important to bear in mind that we cannot reckon in the case of colloidal solutions with the degree of purity such as is attained in the true solution of a crystalline substance. This is caused in the first place (see p. 501) by the method of preparation, and secondly by the limited possibility of purification, and in many cases by the fact that certain foreign substances are necessary for the stability of the sol. For the phenomena affecting sols hitherto dealt with, such as the Brownian movement, this fact is of no importance since this phenomenon is not directly influenced by foreign substances. In the case of other properties the presence of foreign substances must, however, be given much attention.

(*a*) The Lyophobic Sols

It is the purpose of this book to elucidate as far as possible the general laws of colloid chemistry. But a one-sided view is obtained when only this one aspect of the phenomena is considered, since the chemical peculiarities of the dispersion medium and of the disperse phase are of too great importance in individual cases. Hence, after considering the general properties of sols, the most important individuals or groups of individuals will be discussed separately.

1. General Part

Density, Refractivity, Surface Tension, Compressibility and Related Properties of Lyophobic Sols

As already remarked, sols with water as dispersion medium have been examined to such a preponderating extent that almost all data of importance relate to them. When the contrary is not expressly stated we shall therefore always deal with aqueous sols.

The amount of disperse phase contained in hydrophobic sols is generally small. The most concentrated As_2S_3 sol prepared by Kruyt and van der Spek [1] contained about 75 grams of As_2S_3 in the kilogram of sol, the most concentrated Fe_2O_3 sol (Geffcken [2]) 35 grams per litre, the most concentrated gold sol (Zsigmondy [3]) 1·2 grams per litre; in the case of metallic sols the content is generally about 0·1 per cent., of hydroxide and sulphide sols about 1–5 per cent. These are extremely small molar concentrations; for if we suppose the As_2S_3 particles, which may unhesitatingly be regarded as spherical, to have a radius of 50 $\mu\mu$, which would not be unusual, we have a molecular weight of $8{\cdot}6 \times 10^8$, and thus for the above-mentioned sol containing 75 grams per kilo a molar concentration of about 0·042 micromol (millionths of a mol).

Since further in the case of the hydrophobic sols comparatively little water is taken up by the disperse phase, it is an intelligible and necessary corollary that many properties vary but slightly and hence may be very exactly represented by a linear equation.

Thus the specific volume may be represented to the fifth or sixth decimal place by means of a formula

$$v_S = (1 - x)v_M + xv_D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where v_S is the specific volume of the sol, v_M that of the water, v_D that of the disperse phase, and x the concentration of the disperse phase in parts by weight to parts by weight of sol. This results from measurements by Wintgen [4] on ferric hydroxide, arsenic trisulphide, and antimony trisulphide sols, as also from older data of Linder and Picton [5] and of Dumanski.[6] Within the limits of experimental error v_M is found to be equal to the value for pure water. The specific volume of the disperse phase is, however, generally smaller than the value otherwise obtained for the amorphous substance. The density is therefore greater than that observed directly.

[1] Kolloidzeitschr. **25,** 1 (1919).
[2] Zeitschr. f. physik. Chemie, **49,** 299 (1904).
[3] Lieb. Ann. **301,** 33 (1898).
[4] Kolloidchem. Beihefte, **7,** 266 (1915).
[5] Journ. Chem. Soc. **67,** 71 (1895).
[6] *Dumanski, Zabolinski,* and *Ewsejew,* Kolloidzeitschr. **12,** 9 *et seq.* (1913); **13,** 222 (1913).

Wintgen believes this to be due to the surface pressure, which (see p. 8) is equal to $\frac{2\sigma}{r}$, causing compression in such small particles. Kruyt,[1] however, rightly points out that the probable value of the interfacial tension σ is too small to produce a compression of more than a few parts per thousand. The want of agreement is probably to be accounted for by the density of the amorphous substances in question not being accurately known.

Matters are quite similar as regards the *refractivity*. If dispersion medium and disperse phase do not influence one another, one may assume with Wintgen [2] that the time taken by light to traverse a certain distance in the sol is equal to the sum of the times which it requires to pass through the medium and the disperse phase. An equation is obtained as follows:

$$n_S v_S = k_1(1 - x)n_M v_M + k_2 x n_D v_D. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In this n_S, n_M, n_D are the indices of refraction of sol, dispersion medium, and disperse phase, v_S, v_M and v_D the corresponding specific volumes, x the concentration by weight of the disperse phase to parts by weight of sol, k_1 and k_2 constants. Besides k_1 and k_2, n_M, n_D, v_M and v_D are constant; n_D is generally unknown, so that as a rule the equation

$$n_S v_S = K_1(1 - x) + K_2 x$$

is tested. According to Wintgen this equation holds very exactly for the same sols for which he investigated the density.

The *surface tension* (against air) is not sensibly different from that of water in the case of hydrophobic sols (less than 1 per cent.). This results from measurements by Zlobicki [3] (silver, gold, and platinum sols), Linder and Picton (As_2S_3 sols, 20 gr. per litre; Fe_2O_3 sols, 27·2 gr. per litre [4]), and Freundlich and Leonhardt [5] (V_2O_5 sols). From this behaviour it follows, as will be discussed later (p. 790), that upon hydrophobic sols no solid films are formed, and hence they do not form froth.

The *interfacial tension* against other liquids has, as far as I can discover, not been measured. It is very unlikely that the state of affairs differs from that of the surface tension.

The same is true for the *compressibility*, which, as is well known, is antibatic to the surface tension (see p. 78). The compressibility of the disperse phase will probably be additive to that of the dispersion medium, only its influence will be small on account of the low concentration.

In so far as the disperse phase does not appreciably change the dispersion medium by taking hold of water molecules, and does not itself sensibly dissolve or adsorb gas molecules, the *solvent power* of a sol for a gas will not be different from that of pure water. This is also confirmed by experiment; the solubility of oxygen and nitrous oxide in Fe_2O_3 sols, of CO_2 in As_2S_3 sols (Geffcken [6]) are the same as in pure water. But in the case of those hydrophobic sols which form the transition to hydrophilic ones, such as Fe_2O_3, notable departures from this behaviour appear. Thus Geffcken found that CO_2 in a Fe_2O_3 sol (35 gr. Fe_2O_3 per litre) dissolved much more freely than in pure water; the solubility at 25° amounted to 0·928, while that in pure water was 0·8255.

[1] Kolloidzeitschr. **20**, 239 (1917).
[2] *loc. cit.* p. 365; further also *Wiegner*, Kolloidzeitschr. **20**, 7 (1917).
[3] Bull. d. l'Acad. d. Cracov. 1906, p. 488.
[4] Journ. Chem. Soc. **87**, 1924 (1905).
[5] Kolloidchem, Beihefte **7**, 206 (1915).
[6] Zeitschr. f. physik. Chemie, **49**, 297 (1904).

These results have been confirmed by Findlay and his co-workers.[1] In As_2S_3 sols the solubility of N_2O was equal to that in water; on the other hand, it was somewhat less soluble in Fe_2O_3 than in water, while CO_2 was much more soluble. It is also curious that the solubility does not follow Henry's law, but increases considerably with decrease in gas pressure; for example, in a sol containing 4·7 gr. Fe_2O_3 per litre, from 0·904 at 74 cm. Hg to 1·044 at 25 cm. Hg. The strongly specific behaviour of CO_2 points to a chemical action in which the main chemical valencies are concerned. According to Luther and Krsnjavi[2] CO_2 and Fe_2O_3 probably form a complex anion, which is also formed when Fe_2O_3 is dissolved in bicarbonate solutions. Since the salts of this anion probably diffuse through animal membranes, it would be possible that from a Fe_2O_3 sol, rich in CO_2, iron compounds would diffuse out, while this would not be the case with the pure sol. Of course it is also possible that the complex salt would remain adsorbed upon the colloid particles.

In coarse suspensions of quartz and carbon, Findlay and Creighton[3] found a greater solubility for both CO_2 and N_2O than in water; especially for carbon the absorption could be well represented by the adsorption isothermal, so that the phenomenon is to be interpreted as the adsorption of a gas upon the suspended particles.

It may be remarked that coarse emulsions and suspensions will be quite like lyophobic sols in respect of other properties as well; density and refractivity will be expressed additively, surface tension, interfacial tension, etc., will not be sensibly different from those of the suspension medium. Thus Perrin[4] was able to determine the density of gamboge and mastic emulsions on the assumption that he had insoluble particles in a liquid.

The sols referred to in this section may be generally prepared so pure that the observations are hardly rendered fallacious by foreign impurities. With some properties, such as surface tension and solubility of gases, impurities should make themselves felt by an alteration in the property in question, or by influencing it in the opposite direction. The possibility exists, however, that they might be practically completely adsorbed by the colloid particles, so that their influence would not appear. We can, as will be described later (p. 621), actually prove the adsorption of a foreign substance by its not producing the elevation or depression of the surface tension in presence of the colloid particles that it would produce in pure solution.

The Viscosity of Lyophobic Sols

The viscosity of a liquid in which spherical particles in small number are suspended may be represented by a relation deduced by Einstein[5] in which the influence of these spheres upon the shearing of the liquid is taken into account. The resulting formula was

$$\eta_S = \eta_M(1 + 2{\cdot}5\varphi) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[1] *Findlay* and *Harby*, Kolloidzeitschr. **3**, 169 (1908); *Findlay* and *Creighton*, Journ. Chem. Soc. **97**, 536 (1910); *Findlay* and *Shen*, *ibid.* **101**, 1459 (1912); *Findlay* and *Th. Williams*, *ibid.* **103**, 636 (1913); *Findlay* and *G. King*, *ibid.* **103**, 1170 (1913); *Findlay* and *Howell*, *ibid.* **105**, 291 (1914).

[2] Zeitschr. f. anorg. Chemie, **46**, 171 (1905).

[3] *loc. cit.* under [1].

[4] *loc. cit.* p. 343.

[5] Ann. d. Physik (4), **19**, 289 (1906). See especially also Bancelin, Compt. rend. **152**, 1582 (1911); *Einstein*, Kolloidzeitschr. **27**, 137 (1920). *Einstein* originally gave the numerical factor erroneously as 1 instead of 2·5.

Here η_S is the viscosity of the suspension, η_M that of the pure liquid, φ the volume of the particles in unit volume of the suspension. The striking feature of this equation is, that according to it the degree of dispersity of the disperse phase is without influence; if the volume φ is the same it does not matter whether it is that of a small or large number of particles. This equation is, however, only true for limiting cases; it assumes that the particles are rigid and strictly spherical and that their volume only amounts to a small fraction of the total.

At present it is difficult to judge how far this relation may be applied to suspensions and lyophobic sols. Although the viscosity of colloidal solutions has often been measured, this was usually done with lyophilic sols (cf. p. 539). The sulphur sol investigated by Odén [1] also belongs more to the latter group. Fe_2O_3 [2] and Al_2O_3 [3] are, it is true, to a great degree electrocratic, but as regards their viscosity they are closer to the hydrophilic sols. For testing the Einstein formula, measurements carried out on them are of no use, since the water-content of the colloid particles is great and unknown, so that no estimate can be made of the value of φ. From their behaviour it would, however, appear that apart from the validity or otherwise of the Einstein formula, the water-content of the particles and the resultant "active volume" is of great influence on the viscosity of sols; generally in the sense that with increasing water-content the viscosity increases.[4] Nor can φ be given with certainty for the silver sols whose viscosity was investigated by Woudstra [5]; they were prepared according to the method of F. Wöhler [6] and Muthmann [7] (cf. p. 507), and accordingly contained a certain amount of foreign organic matter.[8]

In all these cases the viscosity increases in the region of small concentrations linearly with the content of disperse phase. The same is true of measurements by Bancelin [9] in mastic and gamboge emulsions. The coefficient in the last-named case is fairly close to that calculated by Einstein, but distinctly larger, 2·9 instead of 2·5. The experiments of Bingham and Durham [10] with suspensions of kaolin, graphite, and other substances fit the Einstein formula in so far as a linear relation could be recognized; but the numerical coefficient did not agree with the theory.

The linear rise in the case of these sols, as of the emulsions investigated by Bancelin, is confined to small concentrations. For higher ones the viscosity-concentration curve is decidedly convex towards the axis of concentration.

The departures from the Einstein formula are probably simply due to the fact that the fundamental assumptions mentioned above are not fulfilled in the case of the sols and emulsions investigated. Apart from the conditions named there is further the frequent influence of the charge of

[1] "Der Kolloide Schwefel." Nov. Act. reg. soc. scient. Upsal., Ser. IV, **3**, No. 4, p. 85 *et seq.* (1913).

[2] *Du Pré Denning*, "Ueber die Viskosität und die magnetische Doppelbrechung des kolloidalen Eisenoxydhydrates." Diss., Heidelberg, 1904.

[3] *Gann*, Kolloidchem. Beihefte, **8**, 63 (1916).

[4] *v. Smoluchowski*, Zeitschr. f. physik. Chemie, **92**, 157 *et seq.* (1918).

[5] Zeitschr. f. physik. Chemie, **63**, 619 (1908).

[6] Lieb. Ann. **30**, 1 (1839).

[7] Ber. d. deutsch. chem. Ges. **20**, 983 (1887).

[8] Metallic sols prepared by *Bredig's* method are so dilute that their viscosity is not different from that of water [*Mifka*, Sitzungsber. d. K. Akad. d. Wiss. in Wien, **120**, IIa, 1173 (1911).

[9] *loc. cit.* p. 367.

[10] Amer. Chem. Journ. **46**, 278 (1911).

the colloid particles on the viscosity of the sol. As will shortly be discussed, sols as we mostly know them are not in equilibrium, but are much more uniform than if they were so, because the particles fall so slowly, sometimes only a few centimetres per year. But the falling of the particles generates a cataphoretic current in the liquid (see p. 247), and this causes the viscosity to be greater, for the potential energy of the falling particles does not merely generate the usual frictional heat, but also Joule heat, produced by the electric current. Hardy [1] already took account of this and believed that the permanence of sols could be mainly attributed to it. *v.* Smoluchowski [2] then calculated the effect and showed that it does indeed increase the stability, but that the falling itself takes place very slowly; it is sufficient in all essential respects for the understanding of the behaviour of the sols. The enlarged Einstein formula, which takes account of this electrical influence, runs

$$\eta_S = \eta_M \left\{ 1 + 2{\cdot}5\varphi \left[1 + \frac{1}{\lambda \eta_M r^2} \left(\frac{D\zeta}{2\pi} \right)^2 \right] \right\} \quad . \quad . \quad . \quad . \quad (2)$$

Here λ is the specific conductivity, r the radius of the particles, D the dielectric constant, ζ the electrokinetic potential difference. The influence of the cataphoretic current is particularly evident when the charge on the particles is large, the conductivity—and hence the content of foreign electrolytes—small, and also the radius as small as possible. It may, however, become very marked already for $r = 150\ \mu\mu$; the factor φ of the Einstein formula becomes in this case 5 instead of 2·5, if we take $\frac{1}{\lambda} = 10^6$ ohms per cubic cm. and $\zeta = 0{\cdot}038$.

A careful investigation of the viscosity of undoubtedly lyophobic sols and suspensions is evidently wanting. In such an investigation it would be important to make use of a method, other than the efflux through capillary tubes, which has hitherto been employed almost exclusively. In the case of lyophilic sols we shall have to return to the question (cf. p. 539) why this method cannot give decisive results. Although the objections to be raised later apply with less force to lyophobic sols, the latter are yet subject to other objections; thus the condition for accurate measurement, that the diameter of the suspended particles is much smaller than the radius of the capillaries, is not fulfilled in the case of the coarser emulsions. Here also the method of Couette, to be described later (p. 541), may be particularly recommended.

Brownian Movement and Diffusion of Lyophobic Sols

The considerations on p. 341 concerning Brownian movement are immediately applicable to lyophobic sols. As already discussed there, many of the most important phenomena were investigated precisely with colloidal solutions, such as the gold sols. The motion of the particles of many of these sols, such as metallic sols, sulphide sols, selenium sols, is under the ultramicroscope very vigorous and beautiful, so vigorous indeed that the measurement of the displacement, as carried out by Perrin on gamboge and mastic emulsions, is rendered difficult. Siedentopf [3] indeed succeeded in directly photographing the movement; but he was obliged to make use

[1] Zeitschr. f. physik. Chemie, **33**, 398–399 (1900).
[2] Kolloidzeitschr. **18**, 194 (1916).
[3] Zeitschr. f. wiss. Mikroskopie, **26**, 391 (1909); Physik. Zeitschr. **10**, 778 (1909).

of a method in which the walls of the experimental trough were only separated by a few μ. Svedberg and Inouye [1] made use of another device. By means of a suitable optical arrangement, the image of a particle seen in the field of the ultramicroscope could be surrounded in its projection upon the drawing surface by a fine ring of light; this ring of light could be moved about by the observer so that the particle always remained surrounded by the ring of light, and its motion, as in Perrin's experiments, followed for a considerable time. The trace of the ring of light was registered on a moving photographic film. From the series of points thus obtained the horizontal displacement of the particle could be measured. The general Avogadro number N was calculated from these measurements in accordance with equation (9), p. 350, as 62×10^{22}.

Westgren [2] measured the distribution in gold and selenium sols according to the hyposmetric formula, and determined the diffusion, and the volume of the particles from the rate of fall by means of Stokes' formula. The diffusion was followed ultramicroscopically; by centrifuging, all the particles were driven against the picein [3] wall of the observation trough, and their diffusion away from it was followed; the vertical distribution of the particles after a certain interval allowed the diffusion constant to be calculated. In order to get the rate of fall, the observation cell with the centrifuged particles on its floor was fixed bottom upwards upon the microscope stage and the descent of the particles away from the bottom followed with the microscope placed horizontally. These measurements gave $N = 60{\cdot}6 \times 10^{22}$. From later and particularly careful measurements with gold sols, in which the volume of the particles varied between $1{\cdot}445$ and $11{\cdot}70 \times 10^{-16}$ c.c., $N = 60{\cdot}5 \times 10^{22}$ was obtained.

The diffusion constant of the particles of a gold sol was also determined macroscopically by Svedberg.[4] He used for this purpose the method of Scheffer [5] and Arrhenius,[6] according to which the sol diffused into pure water above it; after a given time the content was measured spectrocolorimetrically in layers at different heights. At 13·62° for particles of radius $1{\cdot}33$ $\mu\mu$ a diffusion constant in absolute units of $1{\cdot}35 \times 10^{-6}$ was obtained. From the Einstein equation (8), p. 350, the value $N = 58 \times 10^{22}$ was obtained.

A considerable quantity of a uniformly mixed sol containing particles with radii exceeding 10 $\mu\mu$ is in general not in equilibrium. Sedimentation would require that already at a height of 10 cm. the concentration should be only $\frac{1}{10}$ of that at the bottom of the vessel (calculated for particles of 10 $\mu\mu$ radius). On the other hand the rate of fall of such small particles, assuming the validity of Stokes' law, is so minute, only $0{\cdot}4$ $\mu\mu$ per second, that they would take about 7 years to fall 10 centimetres. Years would thus pass before the sedimentation equilibrium was arrived at. Usually other disturbing influences—coagulation by foreign matter derived from the walls of the vessel, or also chemical changes in the colloid particles themselves—prevent this state of equilibrium being reached. On account of these disturbances it is difficult to decide whether the unmistakable formation of layers and clearing of the upper regions of the liquid, which takes place in the

[1] *Svedberg*, "Die Existenz der Moleküle," p. 123 *et seq.*, and Kolloidzeitschr. **7**, 1 (1910).

[2] Zeitschr. f. physik. Chemie, **89**, 63 (1914).

[3] A rubber cement similar to Chatterton's compound.—(*Trans.*)

[4] "Die Existenz der Moleküle," p. 78 *et seq.*

[5] Zeitschr. f. physik. Chemie, **2**, 390 (1888).

[6] *Ibid.* **10**, 51 (1892).

course of months or years with As_2S_3 sols kept undisturbed, is the setting-up of a sedimentation equilibrium or the result of a coagulation and coarsening of the original particles.

The Chemical Nature of the Colloid Particles of Lyophobic Sols

In the case of the phenomena hitherto considered, the influence of the foreign substances contained in sols in addition to the colloid particles could usually be neglected. This is also true for the Brownian movement and diffusion, in which the colloid particles or the change in their concentration is followed directly. But already for the osmotic pressure, which is closely connected with diffusion, and for the processes caused by it, the influence of the foreign substances contained in the sol is decisive. It is therefore convenient to discuss first the chemical nature of colloidal particles and its relation to dissolved impurities.

When one speaks of a gold sol, one is by no means justified in assuming that it contains only gold particles and unaltered water; on the contrary, foreign substances are always present in greater or lesser amount, which are not merely chance contaminations of the sol, but are almost certainly necessary for its stability. Even when chemical reactions are so improbable as in the case of gold, the conditions for adsorption are always the most favourable imaginable. Most lyophobic sols are obtained by the formation of a difficultly soluble phase through the interaction of soluble substances. It was already discussed on p. 339 to what an extent a newly formed, finely divided substance is able to adsorb foreign matter, while it is not able to do so when it is made by finely powdering coarsely crystalline material. Further, on account of the smallness of the resulting gold particles, the newly formed boundary surface is very great—with gold particles of 25 $\mu\mu$ radius an interface of 6 square metres is developed when the sol contains 1 gram per litre. Hence both the dissolved initial substances and the dissolved final products may be adsorbed to some extent.

Here a new concept may be introduced. The concept *colloid particle* characterizes the single particle of the disperse phase according to its osmotic, electrokinetic, and optical behaviour, therefore primarily in respect of its Brownian movement, its cataphoresis, and its ultramicroscopic phenomena. The further concept of the *micella* is intended to characterize, according to Malfitano [1] and J. Duclaux,[2] a single particle of the disperse phase, expressly including its *chemical* behaviour. The concept, although not with this exact meaning, was originated by Nägeli. Of the colloid particles of a gold sol we may say almost without hesitation that they consist of gold. For the micella of the gold sol we must take into account the fact that foreign substances enter into its structure, which largely determine its chemical properties, its electrical charge, and then also its size, etc. Instead of *dispersion medium*, the concept which is complementary to colloid particle, we may speak, in relation to the micella, of the *intermicellar liquid*, which is in equilibrium with the micella.

A lyophobic sol has hitherto only rarely been so accurately investigated that the composition of the micella and of the intermicellar liquid in equilibrium with it could be accurately defined. The most far-reaching data are

[1] Compt. rend. **139**, 920 (1904).
[2] Journ. d. Chim. Phys. **5**, 29 (1907); **7**, 430 (1909).

those of Kohlschütter [1] on silver sols, and of Lottermoser and Maffia,[2] and Pauli and Matula [3] on Fe_2O_3 sols, while further experiments of Lottermoser [4] show particularly plainly upon what the influence of foreign electrolytes actually depends. Kohlschütter analysed his silver sols, obtained by reduction of Ag_2O with H_2, to such an extent that the composition of the micella and of the intermicellar liquid could be given. Unfortunately no measurements were carried out to discover what relation the electrolyte Ag_2O contained in the intermicellar liquid bears at various concentrations to the Ag_2O contained in the micella. Measurements of this kind are found in Maffia's papers, albeit only for a single ion, viz. the Cl′ ion. Although he determined the complete composition of micella and intermicellar liquid less accurately, much may be supplied in this direction from the measurements of Pauli and Matula.

Before these investigations are dealt with, the experiments of Lottermoser will be considered more closely. He prepared AgI sols either by adding a dilute $AgNO_3$ solution to a dilute KI solution, or conversely by allowing dilute KI to flow into dilute $AgNO_3$. In the former case, before the point was reached at which the two substances were present in exactly equivalent amounts, KI was in excess, in the latter $AgNO_3$. Now it was found that the finely divided AgI only remains in colloidal suspension, when either KI or $AgNO_3$ are present in a certain excess. A certain amount of foreign electrolyte was necessary for the stability of the sol. If both substances were present in exactly equivalent amounts, AgI was rapidly precipitated. The distribution of the electrolyte in the sol itself between the micella and the intermicellar liquid was not determined. But the amounts of $AgNO_3$ ($Ag^{\cdot}$ ion) and of KI (I′ ion) adsorbed by large quantities of precipitated AgI were measured. For the $AgNO_3$ the usual adsorption isothermal held, but not for the KI. A saturation was soon reached, followed by a considerable falling off. It would appear, however, that this is not to be referred to the regular behaviour of the adsorption isothermal at higher concentrations (cf. p. 180), but to the AgI becoming coarser and crystalline and hence losing adsorptive power.

In the experiments undertaken in conjunction with Maffia on Fe_2O_3 sols, however, the distribution of an ion, the Cl′ ion, between micella and intermicellar liquid was directly investigated. The intermicellar liquid was separated from the liquid containing micellæ by filtration through collodion sacks.[5] Collodion is a filtering material which allows of many colloid particles being retained, while the dispersion medium filters through. Such a filter, as we shall later discuss more fully (p. 378), is described as an *ultrafilter*. Maffia was able to prove that ultrafiltration itself causes no changes in the micellæ since successive samples of the filtrate showed the same content of Cl′ ion and the same conductivity; further, the results obtained with the ultrafilter could be confirmed by those in which the intermicellar liquid was allowed to enter into equilibrium with the external liquid by dialysis. The ferric hydroxide sols usually contained from the first particles small enough to pass through the ultrafilter. The

[1] Zeitschr. f. Elektrochemie, **14**, 49 (1908).

[2] Ber. d. deutsch. chem. Ges. **43**, 3613 (1910); Maffia, Kolloidchem. Beihefte, **3**, 85 (1911).

[3] Kolloidzeitschr. **21**, 49 (1917).

[4] Journ. f. prakt. Chemie, **72**, 39 (1905); **73**, 374 (1906); Zeitschr. f. physik. Chemie, **60**, 451 (1907); *Lottermoser* and *A. Rothe, ibid.* **62**, 359 (1908).

[5] A method first applied by *Malfitano*, Compt. rend. **139**, 1221 (1904).

sols had therefore first to be fractionally ultrafiltered, until a sol remained behind having sufficiently large particles. The distribution was measured in two ways ; according to the first the initial sol was diluted in stages, and in each sol so obtained the Cl′ ion content of the intermicellar liquid was measured ; since the total content of Cl′ ion was known, the amount of Cl′ ion contained in the micellæ was obtained by difference. In other series of experiments various quantities of chlorides (NH_4Cl and HCl) were added to a sol as poor as possible in Cl′ ions, and the distribution determined in the same way.

In all cases the ordinary adsorption isothermal held, as the following table shows.

TABLE 106 [1]

Distribution of the Cl′ Ions between the Micellæ and the Intermicellar Liquid of a Fe_2O_3 Sol

$$a = 1{\cdot}539\ ;\ \frac{1}{n} = 0{\cdot}268$$

Cl′ Ion Content of the Filtrate (millimol per litre).	$a = \frac{\text{Millimol Cl′ Ion}}{\text{Gram } Fe_2O_3}$ (obs.).	a (calc.).
0·65	1·36	1·37
0·82	1·47	1·46
0·90	1·51	1·50
1·07	1·58	1·57
1·21	1·62	1·62
1·38	1·67	1·68
1·55	1·73	1·73

This behaviour had also been calculated from earlier experiments by J. Duclaux, [2] and was further confirmed by Wo. Ostwald [3] from the conductivity of the intermicellar liquid of ferric hydroxide sols. The adsorption exponent $\frac{1}{n}$ was always small, in most of the measurements smaller than the example chosen for Table 106 ; this has frequently been found for the adsorption of electrolytes (cf. Table 71, p. 202). In agreement with its interpretation as an adsorption is the fact that the distribution equilibrium is rapidly set up, and that the amount adsorbed decreases with rise of temperature. [4]

As an unfortunate source of error in these experiments the following must be mentioned. It does not seem to be excluded that the size of the particles, and hence the adsorbing surface, changes with the content of the electrolyte. This was observed, for example, when NH_4Cl was added to a sol which had been obtained by the action of an ammonium carbonate solution upon a ferric chloride solution ; the well washed sol, which no longer passed a collodion filter, did so upon addition of NH_4Cl. [5]

[1] *Maffia, loc. cit.*, experiment VIII.

[2] Compt. rend. **143,** 296 (1906). Concerning the calculation see the first edition of this book, p. 322.

[3] *van Bemmelen*-Festschrift, p. 267 (1910).

[4] *Malfitano*, Compt. rend. **141,** 660, 680 (1905).

[5] Conversely, in the experiments mentioned above (p. 372) on AgI and KI, the adsorbing surface of the AgI is reduced by the KI.

Ufer [1] has systematically tested whether a Fe_2O_3 sol is really always coagulated by extreme dialysis. This was indeed always the case in glass dialysers, but an influence of the glass walls was not excluded. The sol with least chlorine which was still stable, and could still be conveniently prepared, contained for 1 gm. of Fe_2O_3 0·014 millimol Cl′ ion.

Pauli and Matula [2] have determined the concentration of various ions in Fe_2O_3 sols by means of potential measurements. In older sols of this kind the Cl′ ion concentration may be measured by means of mercury-calomel electrodes, not by silver-silver chloride electrodes. The result was that the amount of chlorine found as ion is less than the total chlorine content of the sol; hence a considerable portion of the chlorine is contained undissociated in the micellæ. The H· ion concentration proved to be not sensibly different from that in neutral solution, nor did it alter appreciably on coagulation by electrolytes. But the Cl′ ion concentration suffered great changes on coagulation by electrolytes.

The chlorine ion is in this case certainly a part of the *active electrolyte*, a term employed by J. Duclaux [3] for that electrolyte which is important for the stability of a sol, as, in the case of the above-mentioned experiments (p. 372) of Lottermoser, $AgNO_3$ and KI for the AgI sol. Even before Duclaux and Lottermoser, Jordis [4] pointed out that foreign electrolytes are important for the stability of a sol.

The behaviour of electrolyte residues in other sols is quite similar to that of the chlorides in ferric hydroxide sols. It cannot therefore be doubted that they also are bound by the micellæ in a similar fashion; everything tells in favour of the validity of the ordinary adsorption isothermal for the distribution, thus, for example, for that of K_4FeCy_6 in sols of copper ferrocyanide and of Prussian blue.[5] In different sols different electrolytes may be considered as active. Frequently those with complex ions of high equivalent weight are preferred. In the case of vanadium pentoxide sols it is an ammonium vanadate, for gold sols apparently an aurate,[6] in sulphide sols hydrogen sulphide or a polysulphide,[7] in ferrocyanide sols potassium ferrocyanide,[8] in lead superoxide sols [9] potassium hydroxide, etc.

The experiments of Kohlschütter [10] bring out relationships, which may perhaps apply generally to many other metallic sols. As was mentioned, he produced an Ag sol by passing H_2 into water containing Ag_2O in fine suspension. The size and nature of the walls of the vessel had a decided effect, a sign that the reduction mainly takes place on them. Sols were only obtained in glass and quartz vessels, not in platinum ones. That glass sensibly adsorbs Ag_2O is known; the important factor is therefore that the reduction takes place in the adsorption layer. This explains why sols prepared in Thuringian and Jena glass vessels differed in colour; those

[1] "Ueber Kolloides Eisenoxyd." Diss., Dresden, 1915.
[2] *loc. cit.* p. 372.
[3] Journ. d. Chim. Phys. **5**, 29 (1907).
[4] Sitzungsber. d. phys.-mediz. Soc. Erlangen, **36**, 47 (1904).
[5] *Henri* and *A. Mayer*, Compt. rend. **139**, 974 (1904).
[6] *Steubing*, Ann. d. Physik (4), **26**, 335–336 (1908), found, for instance, that from a gold sol after the separation of the gold particles by coagulation, a fresh separation of colloidal gold could be obtained by addition of a reducing agent.
[7] *Freundlich* and *W. Neumann*, Zeitschr. f. physik. Chemie, **67**, 538 (1909); *Jordis* and *Schweizer*, Zeitschr. f. angew. Chemie, **23**, 577 (1910).
[8] *Henri* and *Mayer*, Compt. rend. **139**, 974 (1904).
[9] *Bellucci* and *Parravano*, Atti R. Accad. d. Linc. (5), **15**, II, 542 (1906).
[10] *loc. cit.* p. 372.

in Thuringian glass were mostly yellowish brown to rose red, those in Jena glass reddish violet to dark blue. But this difference in colour does not depend upon constituents of the walls appreciably entering into the constitution of the micellæ, but solely upon a different content of Ag_2O, determined by the adsorption relationships on the walls.

The complete estimation of Ag and Ag_2O was carried out as follows. A total amount of the Ag in the sol gave the content of metallic silver plus silver oxide in the micellæ, plus dissolved silver oxide, therefore

$$Ag_M + Ag_2O_M + Ag_2O_L \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The micellæ were flocculated and the amount of silver in the supernatant solution was determined. This is equal to

$$Ag_2O_L \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

if we assume that upon coagulation no Ag_2O passes into solution from the micellæ. The difference between (1) and (2) is therefore the total amount in the micellæ

$$Ag_M + Ag_2O_M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Then a further quantity of the sol was completely reduced in a platinum dish by passing H_2 through it. It was found that in this way both the dissolved silver oxide, Ag_2O_L, as well as that contained in the micellæ, Ag_2O_M, could be removed; it separates in crystals upon the platinum. The silver content of the liquid thus treated is then

$$Ag_M \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The difference between (3) and (4) is the amount of Ag_2O_M in the micellæ. It was found that the sols prepared in vessels of Thuringian glass contained sensibly more Ag_2O than those prepared in vessels of Jena glass. The original micellæ contained with Thuringian glass 33 to 57 per cent. Ag_2O, with Jena glass 4·5 to 14 per cent.

Kohlschütter was further able to show that the silver sols prepared by Bredig by electrical disintegration (p. 509), when analysed in this way, showed the presence of 19 to 52 per cent. of Ag_2O in the micellæ. Kohlschütter inclines to the supposition that it is less a question of an adsorption of Ag_2O by the silver particles than of complex compounds in the sense of Werner's theory. It is doubtful whether a sharp line can at all be drawn between the two phenomena. But it would be important for the comprehension of many other phenomena to know whether the distribution of Ag_2O between micellæ and intermicellar liquid obeys the rules of adsorption or not.

This result may doubtless be generalized without hesitation. Most metallic sols will therefore contain metallic oxides in smaller or larger amount; for example, in the electrical disintegration of metal in water the conditions are undoubtedly favourable at the high temperature for the decomposition of the water and production of oxides. Nor is oxidation by the air impossible. This is also true for the sols of the platinum metals. According to experiments by Graeser [1] platinum disintegrated in the presence of oxygen always contains oxygen, and Beans and Eastlack [2] point out that in the disintegration of platinum (by Bredig's method, p. 509) the conductivity

[1] "Experim. Beiträge z. Kenntnis der optischen Eigenschaft. d. Oxyde einiger edler Metalle." Diss., Leipzig, 1903.

[2] Journ. Amer. Chem. Soc. **37**, 2667 (1915).

increases more rapidly than in the case of gold; this they explain by the more easily oxidized platinum forming more oxide. But that also in the case of gold an active electrolyte is necessary is shown by the fact that according to the latter investigators, besides alkali, also chlorides, bromides, and iodides favour sol formation by disintegration, substances therefore with which complex gold compounds are easily formed; but fluorides, nitrates, chlorates, and sulphates have no favourable effect.

The Osmotic Pressure of Lyophobic Sols: Dialysis and Ultrafiltration

As already remarked, in the case of lyophobic sols the presence of foreign substances, especially of active electrolytes, renders the measurement of osmotic pressure difficult, and also of the phenomena depending upon it—the lowering of vapour pressure and of freezing-point, and the elevation of the boiling-point. In all these phenomena, the sum-total of foreign molecules, whether present in true or in colloidal solution, makes itself felt, and not merely the colloid particles alone. One might hope to separate out the osmotic action of the micellæ by deducting that part of the total effect due to the foreign substances. But as a rule the nature and amount of the latter, and their distribution between micella and intermicellar liquid, is not known with sufficient accuracy.

Our knowledge of the osmotic pressure and the phenomena connected with it is therefore still uncertain and lacking in precision. Undoubtedly the *lowering of vapour pressure*, the *lowering of the freezing-point* and the *elevation of the boiling-point* of lyophobic sols are small. Freezing-point experiments, in which the depression rarely exceeded a few thousandths of a degree, have been made by

Picton [1] with an As_2S_3 sol.

Krafft [2] with Fe_2O_3 and Al_2O_3 sols.

Bruni and Pappadà [3] with sols of Prussian blue, Fe_2O_3 and Cr_2O_3.

Whitney and Blake [4] with gold sols.

J. Duclaux [5] with sols of Fe_2O_3 and ThO_2.

Dumanski [6] with sols of Fe_2O_3 and many others.

The *osmotic pressure*, on the other hand, makes itself easily and frequently felt, for example when sols are dialysed against pure water; a considerable absorption of water by the sol is then often observed. It is however *a priori* not clear whether this action arises from the colloid particles themselves or from residual electrolyte which has not diffused sufficiently rapidly through the membrane. The molar concentration of the colloidal particles would itself suffice to bring about a measurable pressure. Thus, for example, with an As_2S_3 sol of 50 grm. per litre and having particles of radius 2·5 $\mu\mu$, we would have a concentration $c = 0{\cdot}6$ micromol per litre, from which, by means of the formula

$$P = RTc \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

a pressure of about 15 cm. of water may be calculated.

Measurements of the osmotic pressures of sols have been mainly carried

[1] Journ. Chem. Soc. **61**, 146 (1892).
[2] Ber. d. deutsch. chem. Ges. **32**, 1614 (1899).
[3] Atti R. Accad. d. Linc. (5), **9**, I, 354 (1900).
[4] Journ. Amer. Chem. Soc. **26**, 1363 (1904).
[5] Compt. rend. **148**, 714 (1909).
[6] Kolloidzeitschr. **8**, 232 (1911).

out by J. Duclaux [1] and especially by W. Biltz.[2] The latter used as membrane a collodion sack, which was carried by a framework of platinum wire gauze. To this an ascending tube was attached, and further an arrangement to enable the contents of the sack to be stirred. Biltz (see p. 551) chiefly examined lyophilic sols. Among electrocratic sols he, like Duclaux, really only investigated that of ferric hydroxide. With this he found it impossible in dialysis against water to get a distinct and constant osmotic end pressure. The time change in the osmotic pressure, which passed through a maximum, could be explained as arising from the electrolytes in the sol; these diffused so slowly through the membrane, that they produced temporarily a considerable osmotic pressure. J. Duclaux measured the osmotic pressure of ferric hydroxide sols against the intermicellar liquid which he had obtained by filtration through a collodion filter. He further assumed that the composition of the sol does not change by filtration. He too obtained no definite results in his experiments, which only extended over a comparatively short time.

If one could succeed in any one case in determining the actual osmotic pressure of the colloid particles, it would be a further means of determining N. From equation (1) we can obtain c, and c is also given by the equation

$$c = \frac{m}{\mathrm{N}.\frac{4}{3}\pi r^3(\varrho - \varrho_f)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here m is the weight of colloidally dissolved substance, r the radius of the spherical particles, ϱ their density, and ϱ_f the density of the intermicellar fluid.

Experiments of this kind with lyophobic sols have not yet been successful.

Dialysis depends, as has already been said, upon the impermeability of membranes, such as parchment and collodion, to the colloid particles, and their permeability to liquids and truly dissolved substances. The process has retained its importance for colloid chemistry undiminished since the time of Graham.[3] It is still always employed to recognize a colloidal solution as such and to free it from dissolved impurities. In order to determine whether a solution is colloidal or not, it usually suffices to place it in a collodion sack or in the dialysis thimbles of parchment paper which are articles of commerce, and to immerse this in the pure dispersion medium. By means of the colour or a suitable analytical method it may then be ascertained whether the disperse phase diffuses through or not. For the purification of sols the old Graham dialyser is still frequently employed; the dialysing membrane is attached to a bottle in place of the bottom, removed by cracking it off; the sol is put into the bottle, which dips into a dish containing the pure dispersion medium. The dialysis is more rapid and thorough when the surface of the dialysing membrane is as large as possible compared with the volume of the colloidal solution. A very convenient form is that of the star dialyser devised by Zsigmondy and Heyer.[4] A round plate of ebonite has an opening in the middle, ribs spread out radially from it to an edge which runs round the plate. Upon this edge fits an ebonite ring; the

[1] Journ. d. Chim. Phys. **7**, 405 (1909).

[2] *W. Biltz* and *v. Vegesack*, Zeitschr. f. physik. Chemie. **68**, 357 (1910). Here also directions for the preparation of collodion sacks.

[3] *loc. cit.* p. 1.

[4] Zeitschr. f. anorg. Chemie, **68**, 169 (1910).

collodion membrane is attached to it, and rests between the edge of the plate and the ring upon the radial ribs. The sol rests upon the membrane inside the ring, the external liquid streams continually through the middle hole in the plate, past the membrane, and out through openings in the edge into a funnel, within which the whole arrangement rests. Marks Neidle [1] recommends an arrangement in which dialysis is accelerated by rise in temperature, and Thoms [2] increases its rate at ordinary temperature by moving the liquid or the membrane in the liquid. In his method the liquid to be dialysed and the external liquid are contained in hemispherical glass vessels which may be pressed together at ground edges, between which the membrane lies; the dialysis vessel is turned either about an axis lying in the plane of the membrane or about one at right-angles to it.

A very effective method for purifying colloidal solutions, which is also employed technically (cf. p. 644), consists in combining dialysis with electrosmosis and electrolysis.[3] The sol is contained in a vessel enclosed between diaphragm walls which prevent the passage of colloid particles, while the solvent containing electrolytes is forced through the pores by electrosmosis, and ions are forced through by electrolysis. If necessary, pure dispersion medium may be allowed to flow with the proper velocity to the sol and also to the external compartments containing the electrodes. The correct choice of the diaphragm is of importance; those which assume a negative charge hinder the passage of the anions, those with a positive charge that of the kations. It is therefore necessary to take for the middle chamber diaphragms of different kinds, negative at the side towards the kathode, and positive at the anode side (cf. p. 264).

In order to separate the disperse phase from the dispersion medium, or to obtain a part of the intermicellar liquid as such, a pressure is necessary which will force the dispersion medium through a semipermeable membrane which holds back the colloid particles. Ordinary filters have, as is well known, too large pores for this; indeed, "running through the filter" is often the first sign that we are dealing with a colloidal solution. According to experiments by Bechhold [4] hard filter papers still have pores greater than 1 μ, and hence the same membranes must be employed as for dialysis. It has already been said (p. 372) that collodion membranes are frequently employed, and that this method is called *ultrafiltration*. In individual cases it has been employed for a long time, first apparently by C. J. Martin.[5] It has been systematically employed by Bechhold [6] in particular. He pursued the idea of altering the pore size of the filter membranes by making them of gels of different concentration.

Ultrafiltration is the reverse of osmosis. Since the osmotic pressures occurring in the osmosis of colloidal solutions is small, only small pressures should be required for ultrafiltration. This appears to be contradicted by the fact that high pressures have been frequently employed in ultrafiltration with very low yield. This is due, however, as Wo. Ostwald [7] points out,

[1] Journ. Amer. Chem. Soc. **38,** 1270 (1916).
[2] Ber. d. deutsch. chem. Gesellsch. **50,** 1235 (1917); **51,** 42 (1918).
[3] *Ruppel,* Ber. d. deutsch. pharm. Ges. **30,** 314 (1920).
[4] Zeitschr. f. physik. Chemie, **64,** 332 (1908).
[5] Journ. of Physiology, **20,** 364 (1896). A historical survey is given by *Wo. Ostwald,* Kolloidzeitschr. **23,** 70 (1918).
[6] Zeitschr. f. physik. Chemie, **60,** 257 (1907); **64,** 328 (1908); Kolloidzeitschr. **1,** 107 (1906); **2,** 3 (1907).
[7] Kolloidzeitschr. **23,** 68 (1918).

to the fact that we are often dealing with lyophilic sols, in which, as we shall see later (p. 551), special conditions obtain. With lyophobic sols, such as of As_2S_3 and selenium, a considerable quantity of the dispersion medium can be removed from the sol by the convenient methods of Zsigmondy [1] and of Schoep [2] at low pressures in a short time.

Bechhold used filter paper as the framework for his filter membranes; this is soaked in gelatin, which is hardened by formaldehyde, or in a solution of collodion in glacial acetic acid which is gelatinized by water. The permeability of the filter membranes can be altered in stages by raising the concentration of the collodion used in their preparation. Schoep's arrangement is very convenient. He uses collodion sacks, the permeability of which can be increased over a considerable range by addition of castor oil and gelatin. The weight of the sol in the bag suffices to force the dispersion medium through. Zsigmondy's method is also much to be recommended. The arrangement consists of a funnel, a sieve plate, and a ring, which are ground to fit one another and can be clamped together liquid-tight; upon the sieve plate rests a paper filter, upon that a membrane of collodion, which also covers a part of the edge of the funnel. The funnel passes into a filter-flask which is connected to a water pump. Instead of the collodion membrane Zsigmondy and Bachmann [3] later introduced special filters of graded permeability, which are sold as membrane filters by the firm of de Haën. Wegelin [4] recommends an arrangement for purifying sols in which the colloid particles are washed upon the ultrafilter with the dispersion medium; this is allowed to pass through the filter from below against gravity.

Optical Properties of Colloidal Solutions. The Tyndall Phenomenon

As in the case of the Brownian movement, the optical properties of sols depend mainly upon the properties of the colloid particles themselves, so that their investigation has greatly advanced colloidal chemistry, and will continue to do so still further.

Colloidal solutions are already in their appearance more or less distinct from true solutions. It is as if they have a weak fluorescence. If a powerful beam of light be passed through a sol in a dark room, its path may be plainly followed from a direction at right-angles.

Until recently it was supposed that this phenomenon differed fundamentally from ordinary fluorescence because the light radiated sideways is very decidedly polarized, while this is not the case with fluorescent light. But Weigert [5] has recently shown that ordinary fluorescence is also polarized to a certain extent. Fluorescence only differs from the diffraction of light observed with sols in that according to Stokes' rule fluorescent light has a different colour, a longer wave-length than the light of shorter wave-length exciting it, while other laws hold for the light diffracted in sols. In order therefore to decide whether we are dealing with a fluorescence, we must always go back to Stokes' rule.

Matters are simplest when a sol is investigated with particles consisting of a feebly absorbing insulator, such for example as a mastic emulsion with very fine particles of as uniform size as possible. The light radiated side-

[1] Zeitschr. f. angew. Chemie, **26**, 447 (1910).
[2] Bull. d. l. soc. chim. d. Belg. **24**, 354 (1910); Kolloidzeitschr. **8**, 80 (1911).
[3] Zeitschr. f. anorg. u. allgem. Chemie, **103**, 119 (1918).
[4] Kolloidzeitschr. **18**, 225 (1916).
[5] Verhandl. d. deutsch. phys. Ges. (3), **1**, 100 (1920).

ways from this sol has a fine blue colour. If we illuminate with polarized light, the oscillations of which lie in the plane of the paper, in the manner indicated in Fig. 85, the path of the light ray in the sol can only be clearly recognized from the front and from behind, and the polarization is the same as that of the incident light. From above and below, on the other hand, the path is invisible. If the incident light is unpolarized, its path may be seen from all sides, but the light emerging sideways is polarized, its electrical vector lying in a plane at right-angles to the entering ray of light. The phenomenon is called after Tyndall,[1] who was the first to investigate it thoroughly and to recognize its peculiarities.

J. W. Strutt [2] (Lord Rayleigh) showed that it must necessarily occur when light meets upon its path particles which are small compared with its wave-length; this holds for the particles of a colloidal solution. A reflection or refraction in the true sense cannot occur, for these assume surfaces and volumes the dimensions of which are multiples of the wave-length. The lateral scattering of light, as actually observed, can be made intelligible according to Strutt by assuming that the luminous ether has an increased inertia, as it were, due to the particles. If we are dealing with linearly polarized light falling upon insulating, feebly absorbing particles, one would have to imagine, in order to compensate the disturbance due to the particles, sufficiently large periodic additional forces acting upon the particles, which would obviously have to act in the direction of vibration of the light. Equally great, but in the opposite direction, therefore, must be the action exerted by the particles on the light, since there are no additional forces present; that is to say, a periodic disturbance of the same direction of vibration as that of the light arises. This is now propagated in all directions except in the direction of the vibration itself; for in this direction there is no transverse component. This evidently agrees in every way with the above-described behaviour of sols upon illumination with polarized light.

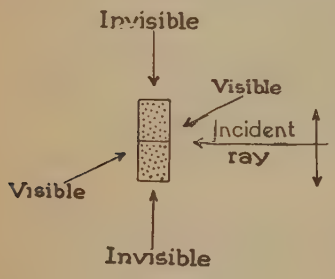

Fig. 85.

The numerical dependence of the intensity of the scattered light upon the size of the particles and the wave-length of the impinging light may be deduced according to Strutt by means of an argument from dimensions. It is very simple and intelligible upon the elastic theory of light, which may be employed without objection, since Strutt [3] showed the electromagnetic theory of light leads to the same formulæ. If one considers a vibration at a distance x from a disturbing particle of volume v, and denotes with i the ratio of the amplitude of the scattered light to that of the incident, then i may depend upon the following quantities; first upon x and v, then upon the velocity of light c, the wave-length λ, and the hypothetical densities d and d' of the disturbed and undisturbed ether. Of these c is the only quantity dependent upon time. Since i is independent of the time, c cannot occur in the expression for i. d and d' are the only quantities in which the dimension of mass enters; since i as a ratio is independent of mass,

[1] Phil. Mag. (4), **37**, 384 (1869).
[2] Phil. Mag. (4), **41**, 107, 274, 447 1871).
[3] Phil. Mag. (5), **12**, 81 (1881); **47**, 375 (1899).

d and d' can only occur as a ratio in the expression for i. Regarding the remaining quantities, the simplest assumption is that the disturbance increases with the size of the particles, and decreases with the distance; hence

$$i = f\left(\frac{v}{x}\right).$$

In order to make i dimensionless, the square of a length must further enter into the denominator; since the only magnitude not yet considered is λ, the wave-length, we finally obtain

$$i = f\left(\frac{v}{\lambda^2 x}\right).$$

The intensity of the light is proportional to the square of the amplitude, hence we get

$$J = \varphi\left(\frac{v^2}{\lambda^4 x^2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Hence *the intensity of the light scattered is directly proportional to the square of the size of the particles, and inversely proportional to the fourth power of the wave-length.* Small wave-lengths are therefore greatly preferred, which explains the blue colour of the scattered light. By transmitted light a colloidal solution of this kind with non-absorbing particles is yellowish red, since the light in passing through loses a great deal of its rays of shorter wave-lengths through lateral scattering. The yellowish red colour of such sols as mastic [1] and sulphur,[2] is entirely due to the Tyndall phenomenon.

The complete formula arrived at by Rayleigh [3] runs

$$J = \frac{9v\pi^2 v^2 A^2}{\lambda^4 x^2}\left(\frac{n_1^2 - n^2}{n_1^2 + 2n^2}\right)^2 \sin^2 \alpha \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here J is the intensity of the scattered light, A the amplitude of the entering light, n and n_1 the indices of refraction of dispersion medium and particles, v the number of particles contained in unit volume, α the angle between the direction of vibration of the polarized incident light and the direction of the diffracted ray, v^2 the mean square of the volume of the particles v; x and λ have the signification already given. The intensity in the main direction at right-angles to the path of the original light is

$$J_0 = \frac{9v\pi^2 v^2 A^2}{\lambda^4 x^2}\left(\frac{n_1^2 - n^2}{n_1^2 + 2n^2}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and the total diffracted radiant energy

$$H = \frac{24v\pi^3 v^2 A^2}{\lambda^4} \cdot \left(\frac{n_1^2 - n^2}{n_1^2 + 2n^2}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If we illuminate with unpolarized light, the state of polarization of the diffracted light varies with the angle of observation and the size of the particles. With very small particles, the light diffracted at right-angles to the original direction is completely polarized; at all other angles the proportion of light polarized decreases symmetrically towards the direction of entry and exit of the original beam. For larger particles, the diameter

[1] See, for instance, *Abney* and *Festing*, Proc. Roy. Soc., London, **40**, 378 (1886); *Lampa*, Ber. Wien. Akad. d. Wiss. **100**, IIa, 730 (1891).

[2] *Keen* and *Porter*, Proc. Roy. Soc. London, **89A**, 370 (1914).

[3] Phil. Mag. (5), **47**, 377 *et seq.* (1899).

of which approaches the wave-length of visible light, the maximum of polarization is displaced, that is, the angle at which the light contains a maximum proportion of polarized light; the angle becomes greater, the polarization maximum approaches the direction of exit. Also the total amount of light radiated laterally is displaced in the same direction, that is, much more light is scattered in a direction nearer to the direction of exit. Rayleigh [1] examined this phenomenon with fine sulphur sols, such as are obtained by acidifying thiosulphate solutions; as the particles gradually became larger, the displacement of the maximum of polarization and the amount of light radiated laterally could be plainly recognized.[2]

The intensity of the Tyndall light may be used to determine colorimetrically the content of sols of the same kind. A useful arrangement is the *Tyndall meter* described by Mecklenburg and Valentiner.[3]

Tyndall Phenomenon and Colour of Lyophobic Sols with strongly absorbing Metallic Particles

The above considerations apply to non- or only weakly absorbing insulating particles. That matters are considerably different for metallic conducting particles follows at once from the colour of the sols containing such particles; they are by no means all yellowish red by transmitted light, bluish by scattered light, but show peculiar, varied, and brilliant colouring; thus many gold sols are deep ruby red by transmitted light, others violet or blue, silver sols red, buff or greenish brown, platinum sols brownish black, and so on.

It was not clear *a priori* how Rayleigh's theory was to be extended. J. J. Thomson [4] carried out the deduction upon the assumption that the metallic particles were to be regarded as perfect conductors, and the theory of Ehrenhaft [5] depends upon the same view; he regarded the action of the metallic particles as one of resonance. The incorrectness of this view was shown both theoretically and experimentally.[6] On the other hand, a good representation of the phenomena was arrived at by introducing into Rayleigh's formula in place of the ordinary indices of refraction the complex indices of refraction of the metals, and indeed those indices of refraction which are obtained from measurements on the ordinary metals. It was in no way necessary to assume all sorts of amorphous forms, in order to explain the different colours of the sols of one and the same metal. These deductions were made by Maxwell Garnett [7] and Mie.[8] Mie limited himself in his theory to *spherical* particles. He compared his calculations with

[1] Phil. Mag. (5), **12**, 95 *et seq.* (1881).

[2] The *Tyndall* phenomenon is the fundamental phenomenon of *Goethe's* colour theory. Cloudy media are reddish against a bright background, blue against a dark one. The circumstance that the physicists of the beginning of the nineteenth century could not explain the phenomenon and scarcely made an attempt to explain it, although the phenomenon kept on presenting itself to capable observers, is also an intelligible reason why *Goethe* was so contemptuous and distrustful of the physicists.

[3] Zeitschr. f. Instrumentenkunde, **34**, 209 (1914); *Mecklenburg*, Kolloidzeitschr. **14**, 172 (1914); **15**, 149 (1914); **16**, 97 (1915).

[4] "Recent Researches in Electricity and Magnetism," p. 437 (1893).

[5] Ann. d. Physik (4), **11**, 489 (1903).

[6] *F. Pockels*, Physik. Zeitschr. **5**, 153, 460 (1904); *Ehrenhaft, ibid.* **5**, 387 (1904).

[7] Phil. Trans. Roy. Soc. London, **203**, 385 (1904); **205**, 237 (1906).

[8] Ann. d. Physik (4), **25**, 377 (1908); further also Lampa, Ber. d. Wien. Akad. d. Wiss. **118**, IIa, 867 (1909); *Schirmann, ibid.* **127**, IIa, 1559 (1918).

measurements by Steubing [1] of gold sols, and used the complex refractive indices from the experiments of E. Hagen and Rubens.[2]

Some of Steubing's main results are represented in Figs. 86 and 87. Fig. 86 relates to a *red* gold sol with particles of radius about 25 $\mu\mu$, prepared by reduction of a gold salt with hydrazine in hot solution; Curve 1 relates to the absorbed light, the absorption coefficients being calculated for equal quantities of gold, Curve 2 to that radiated laterally, in fractions of the light absorbed, likewise referred to equal amounts of gold. The abscissæ are the wave-lengths λ. It will be seen that it is mainly the absorption of light by the gold particles which causes the colour of the sol. The light radiated laterally only constitutes a small fraction. The sol is red on account of the strong absorption in the green (maximum at 530 $\mu\mu$). In agreement with this, Mie calculated that a gold sol with approximately spherical particles of radius 20 $\mu\mu$ would show a decided maximum of absorption at about 530 $\mu\mu$. The absorption curve should fall off rapidly towards the red side of the spectrum, and still more rapidly towards the blue; the radiation should be decidedly less than the absorption, and also show a maximum at about 530 $\mu\mu$.

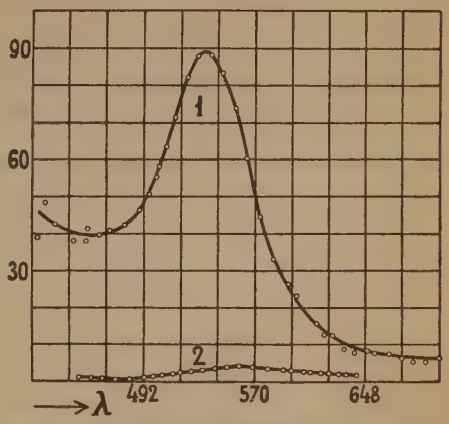

Fig. 86.—Absorption Coefficient and Amount of Light radiated laterally by a red gold Sol.

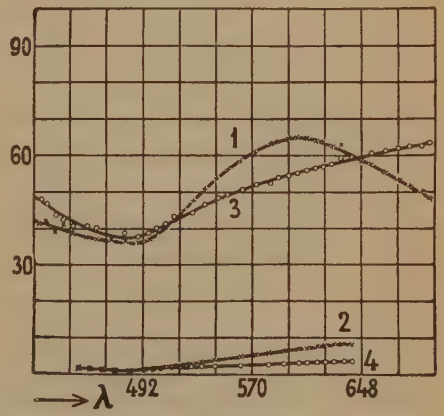

Fig. 87.—Absorption Coefficient and Amount of Light radiated laterally by blue gold Sols.

In Fig. 87 absorption and radiation curves are shown for two *blue* gold sols; curves 1 and 2 relate to a gold sol prepared by shaking from the sediment of a sol which had stood; it therefore contained particles which had been formed by coagulation from still smaller ones. They were not themselves large (radius about 30 $\mu\mu$). Compared with the red sol the maximum is much flatter and decidedly displaced towards the red side of the spectrum (hence the blue colour). Also the lateral radiation is much stronger, likewise especially upon the red side of the spectrum; hence the sol radiates much lateral light of a reddish brown colour. This also agrees very well with Mie's calculations. He finds with increasing radius of spherical particles a decided flattening and displacement of the absorption

[1] Ann. d. Physik (4), **26**, 329 (1908).
[2] Ann. d. Physik (4), **8**, 1, 432 (1903).

maximum towards the red side of the spectrum. The radiation also increases more strongly with the increase in size of the particles. Measurements by Pihlblad,[1] on fairly monodisperse gold sols (that is, sols with particles of uniform size) having particles of diameters between 17 and 152 $\mu\mu$, also agreed well with Mie's theory.

From these calculations it may be concluded that red, weakly radiating sols must contain approximately spherical particles with a radius under 40 $\mu\mu$, while sols with larger particles are blue and radiate more strongly. The cause of this behaviour lies in the fact that gold has an absorption maximum in the green, a reflection maximum in the yellow. With small particles absorption preponderates, hence the red colour of fine-grained sols. With larger particles reflection increasingly predominates, hence the increase in radiation and the displacement of absorption toward the red end of the spectrum. That a sol the particles of which have resulted from the aggregation of smaller ones producing a red colour will have to a large extent the properties of a blue sol of this kind, is but likely; the sols which have become blue by coagulation (cf. p. 416) belong to this group. Experiments of Lampa[2] and Frl. Robitschek[3] also show that violet gold sols upon centrifuging out the coarser particles become reddish.

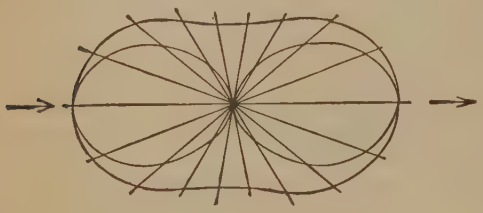

Fig. 88A.

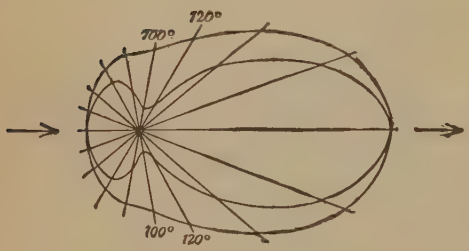

Fig. 88B.

With this one kind of blue sols, however, the possibilities are not exhausted. There are blue sols with other properties, which it is better, however, to consider later on (p. 385).

The polarization relationships do not exhibit any such fundamental difference between insulating and metallic particles. For small particles ($r = 50$ $\mu\mu$ and less) the theory again requires the light radiated at 90° to be completely polarized. For coarser particles the maximum of polarization and the amount of light radiated are displaced toward greater angles, that is, in the direction of exit of the light. The radiation diagrams drawn by Mie are so instructive that they are reproduced in Fig. 88 A and B. At the point from which the radii proceed lies the gold particle from which the Tyndall light proceeds. The outer curve cuts off lengths from the radii proportional to the total diffracted light, the inner curve lengths proportional to the unpolarized diffracted light. One sees how, with infinitely small particles (Fig. 88A), the light is completely polarized at 90°, and how for larger particles (Fig. 88B) the maximum of polarization as well as the total radiation are displaced towards greater angles.

[1] "Lichtabsorption und Teilchengrösse in dispersen Systemen." Diss., Upsala, 1918.
[2] Ber. d. Wien. Akad. d. Wiss. **119**, IIa, 1565 (1910).
[3] *Ibid.* **121**, IIa, 1197 (1912).

Now the theory of Maxwell Garnett and Mie, which relates to particles which are practically spherical, does not include all the cases met with among gold sols. There are sols which have a polarization maximum at 90°, and are therefore composed of particles with a radius less than 50 $\mu\mu$, in which further an aggregation due to coagulation is improbable, and yet these sols are not red in colour, but blue. Such sols were obtained by Steubing, for example, by reducing an $AuCl_3$ solution with hydrazine in the cold. In Fig. 87, Curves 3 and 4, the absorption and radiation curves for such a sol are reproduced; the distinctly different form of the absorption curve and the much lower radiation are easily recognized; the light radiated laterally appears greyish green. Rich. Gans[1] has therefore extended Mie's theory to *non-spherical* particles which are small compared with the wave-length of visible light. He took both greatly flattened and elongated ellipsoids of rotation into account, in the limiting cases, therefore, discs and rods. The result was that for both discs and rods the absorption maximum compared with spherical particles was displaced towards greater wave-lengths. Sols with such non-spherical particles must be blue. In the case of the blue sols with fine particles just mentioned we are probably concerned with small particles not spherical in shape, which for some reason or other have been formed.[2]

It is therefore only in the case of practically spherical particles that the course of the absorption curve produces an absorption maximum in the green, so that the colour of the sols is red. Hence the shape of the particles in red gold sols can only depart slightly from that of the sphere.

Gans has also calculated the polarization relationships for sols with very small non-spherical particles. According to him, in the case of small particles slight deviations from sphericity already result in a small portion of unpolarized light being present along with the polarized at an angle of 90 degrees. Now Steubing[3] has found that with red gold sols also there can always be detected a small amount of unpolarized light at an angle of 90 degrees. A slight departure from the spherical form is hence to be assumed for the particles of these sols also. It may be taken for certain on other grounds (cf. p. 413) that they consist of small octahedral crystals.

Gans[4] was also able to calculate the absorption of silver sols from measurements by Erich Müller[5] upon the assumption of approximate sphericity. With increasing degree of dispersion the colour of silver sols changes from grey green through lilac and red to yellow.[6]

We must pay particular attention to the question: How does the colour of colloidal solutions change when the particles become very small. This does not imply at once that we pass to true solutions of the colloidal substance. This would only be the case if the micellæ were similarly constituted to the solution molecule; if, for example, the micellæ consisted

[1] Ann. d. Physik (4), **37**, 881 (1912).

[2] Another possibility of blue sols with small particles is discussed by *Pogány* [Ber. d. deutsch. phys. Ges. **18**, 298 (1916)]. He uses instead of the optical constants of the metal in bulk the constants of thin layers of gold, which are sensibly different. The values found for thicknesses of 23–12 $\mu\mu$, substituted in *Mie*'s formula, give an agreement with the colour of red gold sols. For still smaller particles the sols should be blue. This seems to me to be contradicted by the fact that amicronic sols (with particles of $2\mu\mu$ diameter) have been made, which were coloured red (cf. p. 504).

[3] *loc. cit.* p. 383.

[4] Ann. d. Physik (4), **47**, 250 (1915).

[5] Ann. d. Physik (4), **24**, 1 (1907).

[6] See *Lüppo-Cramer*, Kolloidzeitschr. **7**, 99 (1910); **8**, 97 (1911); **9**, 73 (1911); **14**, 186 (1914); and *Odén*, Zeitschr. f. physik. Chemie, **78**, 682 (1912).

largely of a pure substance, the solution of non-solvated molecules of the same substance. Svedberg [1] has followed up this question systematically, and has come to the conclusion that in many cases a sol with the finest possible particles has indeed a colour identical with that of the same substance in molecular distribution, that is, in molecularly disperse solution or as vapour. Sols of the alkali metals in ethyl ether had very similar colours to the vapours of the metals in question (see the following Table).

TABLE 107

Colour of highly disperse Sols compared with Colour of molecularly disperse Structures

Alkali Metal.	Colour of Sol.	Colour of Vapour.
Li	Brown	—
Na	Purple violet	Purple
K	Blue	Blue green
Rb	Greenish blue	Greenish blue
Cs	Blue green	—

In other dispersion media the results are less definite, since in them the actual molecularly disperse solution is unknown, and one is concerned in solutions with quite other solution molecules. Nevertheless the following observations confirm what has just been said.[2] Indigo gives in alcohol colloidal solutions, the colour of which, measured spectro-colorimetrically, gradually passes into the colour of the true solutions of indigo in chloroform as the size of the particles diminishes. The same was shown to be true for selenium, aniline blue, indophenone, and azophenone. Also in the case of gold sols it was observed that for very small size of particle the colouring power decreases, and therefore approaches that of the mixed solutions of gold chloride and reducing agent; the absorption maximum, which lies in the ultra-violet for this colourless mixture, shifts quite gradually into the visible region, as the gold sol comes into existence. These results agree with the conclusions of Maxwell Garnett,[3] that exceedingly fine-grained metallic sols should have the same colour as the vapour of the metal itself, and not with Mie's view,[4] that from comparatively coarse particles downwards the absorption should remain practically independent of the size of particle. The rule pointed out by Wo. Ostwald [5] that the absorption maximum moves towards shorter wave-lengths as the degree of dispersity increases, is frequently true, according to Pihlblad,[6] but not always.

The colouring power of colloidal solutions is frequently extraordinarily high; thus the deep yellow colour of the As_2S_3 sol is still recognizable in a layer 1 cm. thick at a concentration of 1 part of As_2S_3 in 800,000 parts of water, the dark red brown colour of Carey Lea's silver sol in a layer of the

[1] Ber. d. deutsch. chem. Ges. **39**, 1705 (1906).

[2] *Svedberg*, "Die Existenz der Moleküle," Leipzig, 1912, p. 5 *et seq.*; Zeitschr. f. physik. Chemie. **65**, 624 (1909); **66**, 752 (1909); **67**, 249 (1909); *Svedberg* and *Pihlblad*, *ibid.* **74**, 513 (1910); further *Svedberg*, Kolloidzeitschr. **4**, 168 (1909); **5**, 318 (1910).

[3] Phil. Trans. Roy. Soc. London, **205**, 241 and 251 (1906).

[4] Ann. d. Phys. (4), **25**, 431 (1908).

[5] Kolloidchem. Beihefte, **2**, 447 (1911).

[6] *loc. cit.* p. 384.

same thickness at a concentration of one part of silver in 5,000,000 parts of water. With red, amicronic gold sols Beer's law was found to hold[1]; and also with monodisperse silver sols prepared according to Carey Lea and sulphur sols[2] prepared by Odén.

The Ultramicroscope[3]

Ultramicroscopic observation is related to the macroscopic Tyndall phenomenon in much the same way as the microscopic observation of the Brownian movement is related to macroscopic diffusion. The ultramicroscope depends upon rendering visible the Tyndall light diffracted from the individual colloid particle. This is attained in the first place by strongly illuminating the particle, for according to equation (2), p. 381, the intensity of the laterally diffracted light increases with that of the incident light. Since the refracted light from a single particle is weak, great care has to be taken to prevent it being masked by stronger external light. The background must therefore be dark. The illuminated layer of the colloidal solution must not be too thick, the sol itself not too concentrated, otherwise the diffraction images generated by individual particles overlap and produce a uniform illumination. Superficially the optical arrangement of the ultramicroscope reminds one of the optical conditions in a dark room, in which a narrow ray of sunlight allows the particles of dust to be seen against a dark background. But an essential difference lies in the fact that the ultramicroscope is not concerned with reflected, but with diffracted light. Each colloid particle recognized ultramicroscopically forms the apex of a cone of light, the base of which is seen as a diffraction disc. No true image of the particle is therefore produced. Strictly speaking only its presence is demonstrated in the first place. In extreme cases, however, such as rod-shaped particles, the shape produces an effect also upon the diffraction image (cf. p. 404), but a spherical particle cannot be distinguished from a cubical or an octahedral one.

An upper limit for the application of the ultramicroscope is imposed by the fact that as soon as the particles have diameters of the same order of magnitude as the wave-length of visible light (about 400 $\mu\mu$ therefore) a reflection takes place at these particles; they shine very brightly in the field of the microscope and mask the Tyndall light of smaller particles. A lower limit is brought about by the intensity of the Tyndall light being proportional to the square of the volume of the particles (see equation (2), p. 381). If the particles are too small to be optically resolved, the field will merely be lit up uniformly and more or less strongly on account of the Tyndall effect. At the limit of resolution the Tyndall light often shows a lively flicker. It is difficult to generalize about the position of this limit, since it not only depends on the strength of the illuminating light, but also upon how greatly the refractive index of the particles differs from that of the dispersion medium (see equation (2), p. 381). The difference between the two refractive indices must be adequate to allow a considerable diffraction of the light to take place at all.[4] If colloid particles and dispersion medium are only slightly different in their refractive power, one observes in the ultramicroscope instead of single diffraction images only a uniform feeble

[1] *Rolla*, Atti R. Accad. d. Linc. (5), **19**, I, 141 (1910).
[2] *Pihlblad, loc. cit.* p. 384.
[3] See King, III B.A. Rep. on Coll. Chem. pp. 31–39.
[4] *Wo. Ostwald*, Kolloidzeitschr. **11**, 290 (1912).

brightening. For the majority of lyophobic sols—the sols of metals, sulphides, etc.—this condition of a sufficiently great difference is entirely fulfilled. They therefore give excellent ultramicroscopic images and allow the full utilization of the possibilities afforded by this powerful instrument. One can reckon on seeing particles down to 10 $\mu\mu$ diameter. How much more unfavourable the lyophilic sols are in this respect, will be discussed later (p. 562).

The colour of the particles in the ultramicroscope naturally corresponds to the colour of the laterally radiated Tyndall light; insulating particles

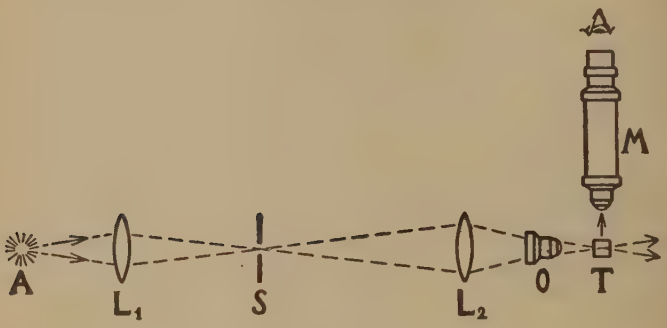

Fig. 89.

radiate a bluish light, small gold particles in red gold sols a green, larger ones in blue sols a brownish, and so on.

Of the various forms in which the ultramicroscope is applied, the following may be described. The instrument originally built by Siedentopf and Zsigmondy [1] was a *slit ultramicroscope*. In this the direction of the illumination is at right-angles to the direction of observation (see Fig. 89). For illumination a powerful source of light A, sunlight or a self-regulating arc lamp, is used; its light falls through a lens L_1, upon a horizontal slit S, of which the lens L_2 and the illumination objective O throw a greatly diminished image in the interior of the trough T; in this is contained the colloidal solution to be investigated. The observation microscope M is so adjusted that this image of the slit falls into the middle of the field of vision. The sol is placed in a trough with quartz windows according to W. Biltz [2] (see Fig. 90), which permits the liquid to be readily renewed, the trough to be cleaned, etc., without the adjustment having to be altered. The advantage of the slit ultramicroscope lies specially in the

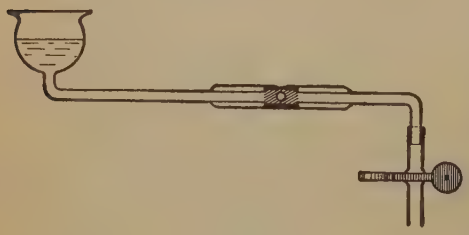

Fig. 90.

[1] *loc. cit.* p. 2.

[2] Nachr. d. K. Ges. d. Wiss. Göttingen, 1904, Heft 4. Frau *Gatin-Gružewska* and *W. Biltz*, Pflüg. Arch. **105**, 115 (1904).

fact that it is comparatively easy to determine the size of the illuminated field from the measurements of the slit and the optical arrangements, which is important for quantitative problems such as the counting of particles, etc. The observation trough is further fairly roomy, so that the behaviour of the particles is followed independently of the influence of the walls. The optical construction is not quite simple, the strength of the illumination might be greater.

A considerably greater strength of illumination was obtained by Zsigmondy[1] with the *immersion ultramicroscope*. In it, illumination objective and microscope objective are brought as near together as possible; the liquid to be investigated can be applied as a drop between the lenses of the two. This arrangement is particularly to be recommended with strongly coloured liquids.

For more qualitative and rapid experiments with maximum illumination those ultramicroscopes are best suited in which the introduction of a condenser suffices to obtain the necessary lateral illumination of the colloid particles. In these the directions of illumination and observation are not at right-angles to one another, but in the same direction. Only the condenser ensures that the light used for illumination shall not fall directly into the microscope, but shall only illuminate the colloidal solution from the side.

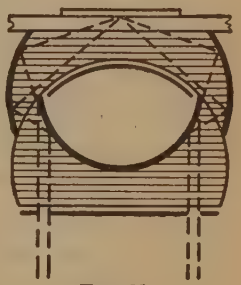

Fig. 91.

As example we may consider briefly the *cardioid ultramicroscope*.[2] The light of a powerful self-regulating arc lamp, rendered parallel by means of a lens, is thrown in the usual manner by means of a mirror through the *cardioid* condenser into the microscope (see Fig. 91). The condenser is opaque in the middle, so that none of this light enters the microscope. Instead it passes through a narrow ring-shaped space, and is so reflected from the condenser surfaces, that upon exit, and crossing itself in one point, it passes through the space below the microscope objective; thereby it leaves at so obtuse an angle, that none of it enters the latter directly. It thus passes through the chamber containing the colloidal solution. This chamber consists of an object glass and a cover glass, both of quartz, between which the sol is contained in a layer 1–2 μ in thickness. Object glass and cover glass can be very carefully cleaned by chemicals, water, alcohol, and finally by ignition in a Bunsen flame. This is necessary, for otherwise reflected light enters the microscope from particles of dust and the like.

The above indicated advantages of this arrangement are coupled with the drawback that quantitative measurements are less simple on account of the very complicated path of the light, since the colloid particles are always comparatively near the walls of the chamber. Likewise experiments in which the action of the electric current or the magnetic field on the particles is observed, are less easy to carry out than with the slit instrument. Each supplements the other with its advantages.

Other types of dark-ground illumination, especially by use of paraboloid

[1] Physik. Zeitschr. **14**, 974 (1913); *Zsigmondy* and *Bachmann*, Kolloidzeitschr. **14**, 281 (1914).

[2] *Seidentopf*, Ber. d. deutsch. physik. Ges. **12**, 6 (1910).

condensers, have been applied to ultramicroscopic purposes by Cotton and Mouton,[1] v. Ignatowsky,[2] Jentzsch,[3] and others.

Kataphoresis in Lyophobic Sols

The main features of kataphoresis in lyophobic sols have already been discussed (p. 244). With electrocratic sols the stability depends chiefly upon electrical influences, and hence they have pronounced charges. They are therefore favourable examples of kataphoresis. According as the particles are positively charged and move towards the negative pole, or are negatively charged and wander towards the positive, we speak of *positive* and *negative* lyophobic sols.

Under ordinary conditions of preparation the sols of a series of hydroxides and oxides are always *positive* sols; such are the sols of aluminium hydroxide, ferric hydroxide, ceric hydroxide, copper hydroxide (made by disintegrating copper electrodes), mercuric oxide (by disintegrating mercury), uranous oxide.[4] *Negative* sols form the great majority; for example, those of sulphur, selenium, tellurium, silver, gold, platinum, and the platinum metals, arsenic trisulphide, antimony trisulphide, mercury sulphide and other sulphides, molybdenum pentoxide, vanadium pentoxide. The kataphoresis has generally been measured macroscopically with the arrangement of Burton (p. 244). Much more exact is the measurement of the velocity of single particles microscopically or ultramicroscopically, especially in the form worked out by Svedberg and Andersson (cf. p. 244). This assumes, however, that the particles can be seen ultramicroscopically. Since with many sols this is not the case, it is often necessary to use macroscopic arrangements. With lyophobic sols the sol usually differs so greatly in appearance from the dispersion medium that a sufficiently sharp boundary between the two can be generated and its movements followed in the Burton tube. With lyophilic sols this is frequently not the case, so that one is obliged to have recourse to the analytical determination of the disperse phase in the electrode space, as in the measurements of ionic transport numbers (cf. p. 564).

Also as regards the sign of the charge of colloid particles, the most important facts have already been given on p. 255. We are naturally dealing with the electrokinetic potential difference ζ, and with a simple course of the ζ curve (Curve 1, Fig. 48, p. 252) a symbasis with ε will be present. The sluggish ion is firmly bound to the wall of the micella, while the mobile ion preponderates in the external mobile water layer. The nature of the active electrolyte residue frequently allows a conclusion to be drawn concerning the sluggish and mobile ions in question. As we shall see later, the nature of the mobile ion is usually revealed in coagulation. It is that ion which is given up to the solution in exchange for an ion of the coagulating electrolyte. With Fe_2O_3 sols the mobile ion is certainly in most cases Cl' [5]; the sluggish ion is either Fe''' or the ion of a basic ferric chloride. With Al_2O_3 sols, which, according to Crum,[6] may be prepared by

[1] Compt. rend. **136**, 1657 (1903). "Les ultramicroscopes et les objets ultramicroscopiques." Paris, 1906.
[2] Zeitschr. f. wiss. Mikroskopie, **26**, 387 (1909).
[3] Verhandl. d. deutsch. physik. Ges. **12**, 975, 992 (1910).
[4] *Samsonow*, Kolloidzeitschr. **8**, 96 (1911).
[5] *Linder* and *Picton*, Journ. Chem. Soc. London, **87**, 1906 (1905).
[6] Lieb. Ann. **89**, 156 (1854).

hydrolysis of the acetate, the acetate ion is probably the mobile ion, $Al^{\cdots}$ or a basic complex ion the sluggish one. This follows from the positive charge of the two sols. From the coagulation the $H^{\cdot}$ ion appears to be the mobile ion for As_2S_3 sols [1]; a complex sulphide ion is probably the sluggish one, hence the negative charge.

Following Zsigmondy,[2] we may represent the constituents of the complex, charged up by the ions, by enclosing them in a square frame, while outside the frame the ions are written; immediately outside the frame the strongly bound sluggish ion (assuming that it is known), further away the mobile ion. The micella of the Fe_2O_3 sol would thus be represented by an expression

$$\boxed{\begin{matrix}Fe_2O_3\\ H_2O,\ Cl\end{matrix}}\ {}^{\cdot}Cl'.$$

That is, the large ion of the micella contains much Fe_2O_3, a great deal of water, and chlorine (cf. p. 374); the sluggish ion is not known with certainty (perhaps $Fe^{\cdots}$); Cl' is the mobile ion. Water should, strictly speaking, always be introduced into the formula, since according to the theory of electrokinesis we are always concerned with a ζ, that is, with the potential difference between a layer of water firmly attached to the micella and an external mobile water layer. In the case of but slightly hydrated micellæ such as those of the metals, perhaps also of the sulphides, this water might be omitted as self-evident; or perhaps better, it might be underlined in the formulæ for the strongly hydrated micellæ, such as those of the hydroxides. The formula for the micella of an As_2S_3 sol would thus be

$$\boxed{As_2S_3}\ S''(H^{\cdot})_2 \text{ or } \boxed{\begin{matrix}As_2S_3\\ H_2O\end{matrix}}\ S''(H^{\cdot})_2,$$

that of Fe_2O_3 sol $\boxed{\begin{matrix}Fe_2O_3\\ \underline{H_2O,\ Cl}\end{matrix}}\ {}^{\cdot}Cl'.$

For metallic sols the formulæ are still very uncertain; in the case of the silver sols investigated by Kohlschütter [3] one might perhaps write

$$\boxed{\begin{matrix}Ag\\ Ag_2O,\ H_2O\end{matrix}}\ {}'H^{\cdot}.$$

These formulæ have an unmistakable resemblance to those of Werner, a resemblance which is probably more than superficial. In limiting cases we certainly have a transition from the loose bond of exchange adsorption to the firmer one of a Werner salt with the ion in the outer sphere of action.

The dependence discussed on p. 257 of the electrokinetic phenomena upon the electrolytes present in the solution is naturally also present in the case of kataphoresis, and has been tested upon hydrophobic sols. Attention may here again be drawn to the fact that with positive CuO sols Burton

[1] *Freundlich* and *W. Neumann*, Zeitschr. f. physik. Chemie, **67**, 538 (1909).

[2] "Zur Erkenntnis der Kolloide," Jena, 1905, p. 168; see also Malfitano, Zeitschr. f. physik. Chemie, **68**, 232 (1910); *Lottermoser*, *ibid.* **70**, 239 (1910).

[3] *loc. cit.* p. 241.

confirmed all the characteristic properties (influence of the valency of the anion, etc.) (see p. 262).

On p. 390 it was stated that all hydrophobic sols hitherto known have a well-defined charge, either positive or negative. This appears to be contradicted by Malarski's [1] experiments. He found that with many sols simple filtration through filter paper, glass wool, etc., sufficed to reverse their charge. But the sol he investigated was of a peculiar kind; a ferric hydroxide sol obtained by the disintegration of iron wire by Bredig's method (cf. p. 509). Here we have (as discussed above for Ag sols) micellæ, in which the iron is only partially oxidized. It may perhaps be represented by the formula

$$\boxed{\begin{matrix}\mathrm{Fe} \\ \mathrm{Fe_2O_3,\ H_2O}\end{matrix}}\ \cdot\mathrm{OH}'$$

If the amount of Fe_2O_3 is small enough, it may distribute itself upon filtration between the micellæ and the filter, and thus decrease to such an extent that it no longer suffices to charge the micellæ positively. This view was confirmed by further experiments of Malarski. He found that, when an Ag sol has its charge reversed by aluminium salts, this now positively charged sol, which lies on the portion CDE of the ζ, c curve (Curve 5, Fig. 49, p. 258), may be given a negative charge again by filtration. Evidently we are again dealing with the distribution of an adsorbed substance, the aluminium ion, between two adsorbents, the silver particles and the filter, and a reversal of charge due to this.

It will be seen that this reversal of charge by filtration presupposes the presence of small amounts of reversing ions. Since this reversal of charge does not by any means proceed very easily (see p. 263)—as a rule only ions of high valency or such as are strongly adsorbed can bring it about—it is intelligible that hydrophobic sols prepared in the usual way have always a charge of fixed sign. Nevertheless it remains advisable frequently to assure oneself by kataphoretic measurements of the charge of a sol under investigation.

The Electrical Charge of a Colloid Particle

From the formula for the kataphoretic velocity (equation (8), p. 244)

$$u = \frac{\zeta \mathrm{HD}}{4\pi\eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

we may calculate the potential difference of the double layer ζ which exists between the wall layer firmly adhering to the colloid particle and the external liquid. If we regard a colloid particle as a spherical condenser we have

$$\zeta = \frac{e(r_1 - r)}{\mathrm{D}rr_1} = \frac{e\delta}{\mathrm{D}r(r + \delta)} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here e is the charge on a single particle, r the radius of the spherical surface and of the inner layer, r_1 that of the outer layer, δ the distance apart of the two layers.

In equation (1) the size of the particles does not appear. For particles of one and the same material the velocity is therefore independent of the

[1] Kolloidzeitschr. **23**, 113 (1918).

size; although the friction increases with the size, u remains unaltered, because the charge also becomes greater. Now it is remarkable that u also does not vary very much for different substances, as was pointed out on p. 257. The smaller the electrolyte content of the dispersion medium, the more frequently does its value lie in the neighbourhood of $3 - 5 \times 10^{-4}$ cm. per sec. for 1 volt per cm. This is evident from Table 81, p. 257. But this is not all; the velocity of the colloid particles has the same magnitude as the speed of most ions, apart from $H^{\cdot}$ and OH', as was already pointed out by v. Smoluchowski.[1]

Thus the speed of the $Na^{\cdot}$ ion at 18 degrees works out at $4{\cdot}4 \times 10^{-4}$ cm. per sec. for 1 volt per cm., that of $K^{\cdot}$ at $6{\cdot}7 \times 10^{-4}$. To a certain extent, therefore, the law holds, that the great majority of electricity carriers appearing in aqueous solutions, whether ions or micellæ, and having radii between 10^{-2} to 10^{-8} cm., have very similar velocities of migration.

For the colloid particles it then follows from equation (1) that they all have an approximately equal potential; ζ amounts to 50 to 70 millivolts. This is, however, as v. Hevesy [2] has shown, the potential to which we may suppose that also the ions are charged. If they too be regarded as condensers, the outer covering of the double layer must be regarded as at infinite distance, since kations and anions in aqueous solution are, as it were, at infinite distances from one another.[3] Hence instead of equation (2) we have the formula for a charged sphere

$$\zeta = \frac{e}{\mathrm{D}r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If a value of 2 to 3×10^{-8} be taken as the probable radius of an ion, we get for ζ a value of 60 to 90 millivolts. Following Hevesy, the further rule may be laid down, that the great majority of carriers of electricity, ions as well as colloid particles, are charged in water to the same potential of 70 millivolts.

Moreover equation (2) passes into (3) for small radii. If the thickness of the diffuse double layer be taken as a few $\mu\mu$—Hevesy takes 5 $\mu\mu$ (see p. 249)—then small values of r may be neglected as compared with δ, and equation (3) follows from (2). If the potential ζ is constant, then $\frac{e}{r}$ is also constant, that is, the ratio of charge to radius is constant for ions and small colloid particles.

For large colloid particles δ may be neglected as compared with r, and hence according to equation (2) $\frac{e}{r^2}$ becomes constant.

Table 108, according to v. Hevesy, shows numerically the increase in e with increase in r for ions (equation 3) and colloid particles (equation 2) and confirms the laws just put forward. As already said, it was assumed that $\zeta = 0{\cdot}07$ volts, $\mathrm{D} = 81$, $\delta = 5$ $\mu\mu$, and the charge of the electron $= 4{\cdot}7 \times 10^{-10}$.

The deductions which follow from these regularities for colloid particles on the one hand and for ions on the other are in many ways antagonistic. The colloid particles have a given size; they must therefore take up in the solution such a charge that ζ acquires a value of about 70 millivolts. The ions, on the other hand, are preformed with their charges in the solid

[1] *loc. cit.* p. 241.
[2] Kolloidzeitschr. **21**, 129 (1917).
[3] See also *v. Smoluchowski*, in "*Graetz*-Handbuch d. Elektr." II, 2, p. 384.

TABLE 108

Radius and Charge of Ions and Colloid Particles

r in $\mu\mu$.	ε from the Equation $\varepsilon = \zeta Dr$ for Ions (in Electrons).	ε from Equation $\varepsilon = \frac{\zeta Dr(r+\delta)}{\delta}$ for Colloid Particles (in Electrons).
0·24	1	1
0·48	2	2·2
0·72	3	3·3
0·96	4	4·6
1·2	5	6·0
2·4	10	14·3
12	50	164
24	100	550
240	1000	47,300

electrolyte. They must, therefore, if they are too small, when the solid electrolyte dissolves, take up as much solvent as is necessary to give them the correct size and with it the correct potential. If, on the other hand, they are originally too large, as with the ions of complicated organic substances, then their potential and migration velocity are correspondingly smaller. A special position is occupied by the $H^{\cdot}$ ion. According to the atomic model of Rutherford and Bohr (cf. p. 37) a hydrogen atom consists of a positive charge around which an electron revolves. The $H^{\cdot}$ ion is a hydrogen atom which has lost its electron. It is therefore simply a charged atomic nucleus, and has a radius of about 10^{-13} cm. It is evident that in view of such a small size the velocity of the $H^{\cdot}$ ion must be much greater. One might perhaps have expected it to be still larger, but this point-like charged nucleus will certainly drag water molecules with it. The $H^{\cdot}$ ion is therefore a particular kind of carrier of electricity. The OH' ion also will have, in accordance with its higher velocity, a considerably smaller diameter than ordinary ions. Many of v. Hevesy's further results, especially those relating to the hydration and size of the ions, do not properly belong to colloid chemistry.[1]

One other point only may be referred to. It may appear curious that in the case of ions a potential ζ is assumed without further question, which none the less presupposes fundamentally a layer of solvent as inner covering. This would only be correct if the ions were always surrounded by an envelope of the solvent, as Kohlrausch[2] assumed at the outset. But quite different observations also support this view. Walden[3] found that the conductivity of an electrolyte in various solvents at infinite dilution

[1] It may be here remarked that quite a different interpretation of the extraordinary mobility of the $H^{\cdot}$ and OH' ions is possible, and has been advanced by *Ghosh* (cf. p. 49) and already earlier by *Danneel* [Zeitschr. f. Elektrochemie, **11**, 249 (1905)] and by *Hantzsch* and *Caldwell* [Zeitschr. f. physik. Chemie, **58**, 575 (1907)]. $H^{\cdot}$ and OH' are just the ions which originate from the solvent, and it might be that perhaps by collisions between them and the molecules of the solvent H atoms and OH groups are continually ionized anew; thereby a transference of charges would be brought about which would be superposed upon the usual *Grotthus* conductivity, and would simulate an unusually large migration velocity of these ions.

[2] Sitzungsber. d. Preuss. Akad. d. Wiss. **26**, 572 (1902).

[3] Zeitschr. f. physik. Chemie, **55**, 207 (1906).

was inversely proportional to the viscosity of the pure solvent. This is only intelligible if, in the motion of the ions in the solution, liquid rubs on liquid, if, in fact, the ions are actually surrounded by envelopes of solvent.

The Conductivity of Lyophobic Sols

The conductivity of lyophobic sols is again a property which it is difficult to measure with precision, since the effect due to the particles themselves is not easy to separate from that due to electrolytes contained in the sol. In any case we have in addition to the ordinary conductivity of the electrolytes that due to the kataphoresis of the particles, as discussed on p. 249. For the latter we have the formula on p. 249,

$$\lambda_\omega = \frac{4\pi\eta\nu r(r+\delta)u^2}{N\delta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The number ν of particles per cubic centimetre is especially important for the magnitude of λ_ω, and ν increases greatly with decrease in the size of the particles ; the indirect influence of the radius, through its great effect on ν, outweighs the direct influence, in the opposite direction, of r on λ_ω, shown by the formula. The quantities η, δ, and u are in comparison less variable.[1]

In order to furnish an idea what values λ_ω may assume, there are given in Table 109 some λ_ω values calculated by v. Hevesy [2] for various values of r, in the case of a gold sol containing 1 gram per litre, with particles having a migration velocity u of about $5{\cdot}2 \times 10^{-4}$ cm. per sec. at a potential gradient of 1 volt per cm. ; δ is assumed equal to 5 $\mu\mu$. No measurements are available which permit of testing formula (1).

Table 109

Conductivity λ_ω due to the Micellæ in Gold Sols of the same Content but with Particles of Different Size

r (in $\mu\mu$).	ν.	ε [3] (in Electrons).	λ_ω (in reciprocal Ohms).
1	$1{\cdot}2 \cdot 10^{16}$	5	$0{\cdot}5 \cdot 10^{-5}$
10	$1{\cdot}2 \cdot 10^{13}$	120	$1{\cdot}2 \cdot 10^{-7}$
100	$1{\cdot}2 \cdot 10^{10}$	8350	$8{\cdot}4 \cdot 10^{-9}$

According to Nordenson,[4] one may estimate that with most metallic sols the small conductivity observed arises from residual electrolyte. He refers especially to the measurements of Whitney and Blake [5] on gold and platinum sols, and those of Burton [6] on gold and silver sols. The same probably applies to Kohlschütter's [7] measurements of silver sols.

[1] It is approximately true, as pointed out by *Nordenson* [Kolloidzeitschr. **16**, 65 (1915)], for the conductivity of disperse systems, which contain the same amounts of substance in different degrees of dispersion, that the conductivities are inversely as the squares of the radii of the particles.

[2] Kolloidzeitschr. **21**, 136 (1917).

[3] See Table 108, p. 394.

[4] *loc. cit.* under [1].

[5] Journ. Amer. Chem. Soc. **26**, 1339 (1904).

[6] Phil. Mag. (6), **12**, 475 (1906).

[7] *loc. cit.* p. 372.

Very much greater conductivities have been found with sols of hydroxides and salts [1] (Fe_2O_3, ThO_2, Prussian blue). With these the difficulty arises that we do not know how large the micellæ are. Nordenson regards it as probable that a, possibly very small, fraction of minute particles, which according to the theory just discussed might cause a considerable conductivity, actually produce this effect. Pauli and Matula [2] accordingly assume a great mobility of the colloid ions in the Fe_2O_3 sol. Here therefore the great migration velocity of colloid ions would already make itself felt, as it frequently appears in the case of hydrophilic sols (p. 566).

If λ_∞ could be measured in a satisfactory manner, then Avogadro's number N could be determined by a new method.

Connected with the conductivity there is the following phenomenon, as Whitney and Blake[3] pointed out. If the kataphoresis is followed macroscopically, particularly with Burton's arrangement, in which the sol is bounded by the pure dispersion medium and the colloid particles move downwards with a sharp boundary surface, it strikes one at once how the originally rather ill-defined surface of separation between sol and water becomes perfectly sharp as soon as the current is switched on ; and it remains sharp, while the particles migrating downwards leave behind them pure dispersion medium. The kataphoretic migration velocity u is proportional to the external gradient of potential (formula (8), p. 244). This gradient of potential is the greater, the smaller the conductivity. Now the conductivity above the sol is less than in the sol itself. In the first place, pure water was originally placed above the sol, and in the second place, the intermicellar liquid remaining behind has a lower conductivity than the sol, in which the conductivity is raised by the micellæ ; in the experiments of Whitney and Blake, for instance, the conductivity of the intermicellar liquid was $3{\cdot}7 \times 10^{-6}$ reciprocal ohms, that of the sol $12{\cdot}7 \times 10^{-6}$. On account of the greater gradient of potential, colloid particles lagging behind will move more quickly, they will be drawn as it were into the sol, and thus the sharp surface of separation is formed.

An effect related to this phenomenon has been described by J. Stock.[4] Quartz powder, which sinks in nitrobenzene or in ether, occasionally does so as a compact mass, which forms a sharp boundary against the supernatant liquid. J. Stock remarks that the velocity of descent of a particle in the free liquid must be greater than that in the suspension, for the potential difference generated by the fall of the particles causes a kataphoretic motion of the particles which tends to raise them, and thus opposes gravity. An estimate of this influence leads, however, to the result that the size of the particles and the degree of uniformity of size must have a distinct influence ; the phenomenon could only appear with suspensions of particles of fairly uniform size. In these experiments the difference in the size of the particles was too great, and this explanation was therefore not straightway permissible. That the gradient of potential influenced the phenomenon was, however, unmistakable. It only occurred when the suspension was

[1] *J. Duclaux*, Journ. d. Chim. Phys. **7**, 405 (1909) ; further also *Maffia*, *loc. cit.* p. 372 ; *Pauli* and *Matula*, *loc. cit.* p. 372. It is a curious fact, mentioned by the last-named investigators, that with Fe_2O_3 sol the conductivity increases so greatly on keeping. Since, however, they could not determine the Cl' ion concentration for the fresh sol, it remains doubtful whether it was not a matter of ions being given up by the micellæ.

[2] *loc. cit.* p. 372.

[3] Journ. Amer. Chem. Soc. **26**, 1348 (1904).

[4] Bull. d. l'Acad. d. Scienc. d. Cracov, 1914, p. 101 *et seq.*

sufficiently concentrated, and when therefore the potential gradient produced by the fall of the particles was sufficiently great. If the potential gradient was lowered, for example by dissolving resin in the ether, the effect could be made to disappear.

The Magnetic Properties of Hydrophobic Sols

These have not yet been systematically investigated. It is worthy of mention that according to W. Hagen [1] Fe_2O_3 in colloidal dispersion has a particularly small magnetic susceptibility.

The Size of Colloid Particles

The ultramicroscope allows of the determination of the size of colloid particles. Not directly, for we have no genuine image formed, but indirectly by various methods.[2] In the first place, the number of particles in a definite volume of the sol may be determined ; such experiments have been described on p. 344. Let the number of particles in one cubic centimetre be ν. Analysis gives the total amount m of the disperse phase contained in 1 c.c. If the density is ϱ, then the volume of the single particle is

$$v = \frac{m}{\nu\varrho} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This method presupposes that the particles are as uniform as possible in size, and that not too many particles are present which lie below the limit of ultramicroscopic visibility. If the latter is the case, the volume comes out too large. Since, however, the mass decreases very rapidly with decrease in size, the resulting error is only considerable if these minute particles are very numerous. Errors may also occur in the analytical determination. We must be assured that the substance determined is present exclusively in the colloid particles and not also partially in solution in the liquid ; thus in gold sols, for example, a sensible amount of gold is frequently present as $Au^{\cdots}$ ions.[3]

If the particles have a lively Brownian movement a great number of measurements is necessary to determine ν (cf. p. 369). It is then more convenient, instead of determining the number of particles, to determine by means of an eye-piece micrometer in the microscope the mean distance x between two particles. In the space x^3 one particle is then contained, in a cubic centimetre $\frac{1}{x^3}$ particles. Hence

$$v = \frac{mx^3}{\varrho}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The conditions presupposed in these measurements are otherwise the same as for the first method.

The volume of a particle in a sol of uniform grain may be approximately determined by means of the Tyndall light, the intensity of which may be measured by the Tyndall meter.[4] If the constants are collected, we may write equation (2), p. 381,

$$J = k\frac{\nu v^2}{\lambda^4}$$

[1] Kolloidzeitschr. **13,** 4 (1913).
[2] *Siedentopf* and *Zsigmondy*, Ann. d. Physik (4), **10,** 16 *et seq.* (1903).
[3] See *Steubing, loc. cit.* p. 383.
[4] *Mecklenburg*, Kolloidzeitschr. **16,** 97 (1915).

Now we have for the concentration c of the sol

$$c = v\varrho$$

(where ϱ is the density of the particles). Hence

$$J = \frac{kvc}{\lambda^4 \varrho} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

With sols of uniform grain the intensity of the Tyndall light is therefore proportional to the concentration of the sol. Since the absolute value of k is not known, v cannot be calculated from equation (3) from the given quantities J and λ. But if we have two sols of equal concentration, but different size of particles, we get

$$\frac{v_1}{v_2} = \frac{J_1 \lambda_1^4}{J_2 \lambda_2^4}.$$

Hence v_2 can be calculated from the given quantities J_1, J_2, λ_1, λ_2, if v_1 has been determined ultramicroscopically. Tyndallmetric measurements of sulphur sols of uniform grain (Odén) gave with small size of particles very satisfactory agreement with values obtained ultramicroscopically; for larger particles unexplained divergences appeared.

In many cases it is desirable to determine approximately the size of a colloid particle contained in a sol. For this purpose experiments are suited which depend upon diffusion effects—in the first place a determination of the velocity of diffusion into jellies. A diffusion of this kind is usually too slow in the case of hydrophobic sols, while it has frequently been employed with success in the case of hydrophilic ones. It will therefore be described later (p. 550). Dialysis and ultrafiltration can however be used for this purpose. A series of filters, say collodion filters, are made, of graded porosity (cf. p. 379), and that filter is found which keeps the particles back completely, while the next filter allows them to pass a little. The filters are standardized with sols of particles of known size. Bechhold [1] has given such a table; collargol sols (particles about 20 $\mu\mu$) are frequently used as reference liquids. The size of the particles changes, however, so easily with the conditions of preparation that it is safer to use for standardization sols the size of whose particles has been determined ultramicroscopically. Here the following source of error must also be taken into account. The fact that the filter may hold back the particles strongly by adsorption may simulate a lower porosity than should be present according to the size of the pores of the filter.

Following Zsigmondy, it is usual to distinguish the particles according to their visibility as *amicrons*, *submicrons*, and *microns*. Amicrons are the particles no longer visible ultramicroscopically; submicrons those visible ultramicroscopically, but not microscopically; microns those visible microscopically. As already remarked, the division between amicrons and submicrons is not a definite one; on the contrary, it depends greatly upon the difference between the refractive indices of the particles and the liquid. When composed of gold, particles of a diameter of about 5 $\mu\mu$ are amicrons. With micellæ containing a great deal of water they may be ten times greater and more. The demarcation between submicrons and microns is given by the resolving power of the microscope. This lies at a particle diameter of about 200 $\mu\mu$.

Here we may take from Zsigmondy [2] a general survey of how the different

[1] Zeitschr. f. physik. Chemie, **60**, 313 (1907).
[2] "Kolloidchemie," 3 Auflage, 1920, p. 25.

properties change with the size of the particles and where certain limits occur.

TABLE 110

0·1 $\mu\mu$	1 $\mu\mu$	10 $\mu\mu$	100 $\mu\mu$	1 μ	10 μ	100 μ	1 mm.
Ultramicroscopic region				Microscopic region			
Particles show Brownian movement				No visible Brownian movement			
Particles pass an ordinary filter paper				Particles are held back by filter paper			
Particles show increased solubility				Particles have ordinary solubility			
True solutions	Colloid solutions			Emulsions and suspensions			
0·1 $\mu\mu$	1 $\mu\mu$	10 $\mu\mu$	100 $\mu\mu$	1 μ	10 μ	100 μ	1 mm.

In the investigation of many questions it remains a troublesome circumstance that sols are generally not uniform in the size of their particles, but contain particles of very different sizes. How emulsions of mastic and gamboge may be made of uniform grain by fractional centrifuging has already been described on p. 344. With most other lyophobic sols this method fails, since the particles cannot be brought into colloidal solution again smoothly and quickly by simply washing out. Fortunately methods are known by which some sols may be prepared of fairly even grain from the start, for which it may be ascertained in which proportion particles of different sizes are present.

It is Zsigmondy's nucleus method [1] which allows fairly uniform gold sols to be prepared with particles of various sizes. The method depends upon the following fact. If a solution supersaturated with gold is not left for the gold to separate spontaneously, but if a large number of minute nuclei are distributed in it rapidly and uniformly, for example by addition of a gold sol with many amicronic particles, then the gold present in supersaturated solution is deposited on these nuclei and a sol is obtained with particles fairly uniform in size. If this coarser sol is now taken as nuclear solution for another supersaturated solution, a sol is obtained with still coarser particles, and this process may be repeated again and again. For the first nuclear solution Zsigmondy usually employs a gold sol obtained by reduction of an $AuCl_3$ solution containing K_2CO_3 with ethereal solution of phosphorus (cf. p. 504). Water distilled through a silver condenser is used. In the ultramicroscope such sols are practically optically empty; they mostly give only a weak Tyndall cone; they therefore contain amicrons exclusively. The supersaturated solution of gold is prepared as follows. The $AuCl_3$—K_2CO_3 solution is prepared with water distilled through a tinned condenser. Instead of ethereal phosphorus solution, a formaldehyde solution is used. With the specially distilled water the red colour of the gold sol appears

[1] Zeitschr. f. physik. Chemie, **56**, 65, 77 (1906).

only $1\frac{1}{2}$ to 2 minutes after adding the formaldehyde ; in this interval the nuclear solution is added, whereupon the liquid becomes red instantaneously.

In a solution supersaturated with silver—ammoniacal $AgNO_3$ solution reduced with formaldehyde—Zsigmondy could also deposit silver upon gold nuclei.

That such sols actually are to a large extent of uniform grain was shown by Westgren.[1] The particles of the sol were allowed to settle for some days in a trough 50 to 70 μ deep. The trough was then turned bottom upwards ; thereupon the particles sank and arranged themselves according to their sizes, since the largest fall fastest. A distribution occurs such as is represented in Fig. 92, A. Then the trough was turned round through 90 degrees (see Fig. 92, B) ; the particles then settled as in Perrin's experiments (cf. p. 343), only somewhat disturbed by diffusion. From the distribution vertically their size can be determined. If we determine further the number of particles present for the bottom layers at different distances a—measured from the bottom of the

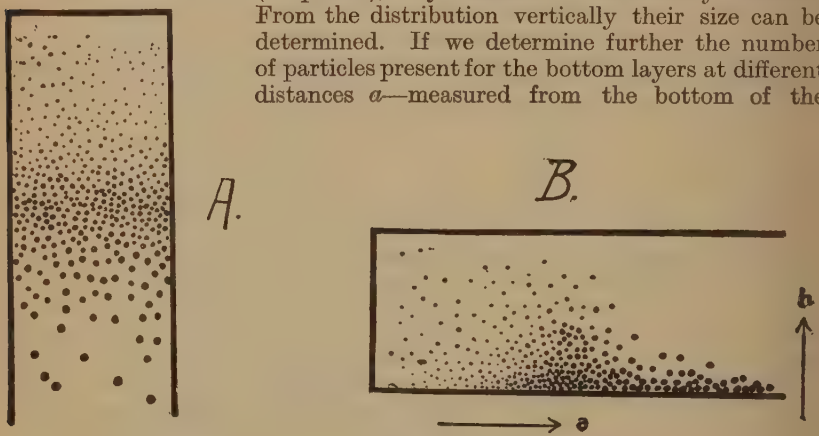

Fig. 92.

trough—then the total number of particles for each size can be calculated. The experiments showed that the particles are distributed according to their sizes upon a Gaussian curve of errors, but the maximum is so sharp that the sol may be regarded as in a high degree composed of grains of uniform size.

On account of their uniformity Zsigmondy's gold sols have been very extensively employed in the investigation of Brownian movement.

The sizes of the amicrons in gold sols have also been successfully determined. The method will, however, be better described later (p. 504).

More difficult than the measurement of the mean size of the particles is the determination of the range of size into which the particles of a sol fall, and how the particles are divided among the various sizes. Svedberg and Estrup [2] have determined ultramicroscopically the rate of falling for a large number of particles of dilute sols and emulsions (Hg sols, gamboge emulsions, milk, etc.), and have deduced their sizes from Stokes' formula. They point out that the displacement during Brownian movement can be used for the same purpose (cf. p. 345).

With suspensions and coarser sols, the particles of which settle sufficiently

[1] Zeitschr. f. anorg. u. allg. Chemie, **94**, 193 (1916).
[2] Kolloidzeitschr. **9**, 259 (1911).

rapidly, a macroscopic method worked out by Odén [1] can be used, by aid of which the distribution of the micellæ according to their size can likewise be determined from Stokes' formula. For this purpose a balance is used, one arm of which carries a plate. This plate dips into a cylindrical vessel so deeply that it is only a few millimetres from the bottom. The vessel contains the suspension, in which the particles are distributed as uniformly as possible. Since a motion of the plate would produce currents in the liquid, which would nullify the measurements, the following arrangement is made. The other pan of the balance is at first a little heavier than the plate; at the moment in which equilibrium is set up, an electrical contact arrangement brings a small weight upon the pan of the balance, by means of which the original condition is restored. This process is repeated every time equilibrium is brought about, and records itself each time upon a moving strip of paper, so that it is possible to determine how great the weight on the balance was at any given time. The whole arrangement must further be placed in a chamber at constant temperature in order to avoid disturbing convection currents. A curve is thus obtained which gives the dependence of the amount settled out upon the time.

If the suspension is uniform the curve is a straight line, for if the particles are small enough Stokes' law applies to them (formula (3), p. 344).

$$u = \frac{2}{9}\frac{r^2(\varrho - \varrho_1)g}{\eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or at constant temperature

$$u = \mathrm{K}r^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where K is a constant. If r is constant, then u is also, hence equal amounts settle in equal times. The weight G settled out after a time t is the greater, the longer the time, the greater the velocity and the total weight G_0 and the smaller the height h which the liquid occupies in the vessel, hence

$$\mathrm{G} = \frac{\mathrm{G}_0 ut}{h} = \frac{\mathrm{K}\mathrm{G}_0 r^2 t}{h} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If

$$t \geqq \frac{h}{\mathrm{K}r^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

then $\mathrm{G} = \mathrm{G}_0$; after the lapse of this time all particles have settled.

If the suspension contains particles of various sizes, we find instead of the straight line a Gt curve, as represented in Fig. 93; it is therefore concave to the axis of t. This curve may be represented as a function of r and t, when we remember that the suspension contains particles of different sizes, and that to each constituent batch of particles of uniform size the equations (2) and (4) may be applied. If one puts $q(r)$ for the percentage amount of particles with radius greater than r, then the percentage amount between the radii r_1 and r_2 is

$$q_1 - q_2 = \int_{r_2}^{r_1} \frac{dq}{dr}\,dr = \int_{r_1}^{r_2} \mathrm{F}(r)dr, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where

$$\mathrm{F}(r) = -\frac{dq}{dr}.$$

[1] Kolloidzeitschr. **18**, 33 (1916); **26**, 100 (1920); Arch. f. Kemi, Mineral. och Geol. **7**, No. 26 (1920); Internat. Mitteil. f. Bodenkunde, **5**, 257 (1915); **9**, 301 (1919).

$F(r)$ gives, as appears from a comparison with the argument on p. 346, the *distribution* of the micellæ according to radii of different sizes; the $F(r)$, r curve is a curve of distribution.

The amount G settled out at time t is thus given by

$$G(t) = t \int_0^{\sqrt{\frac{h}{Kt}}} \frac{K}{h} F(r) r^2 dr + \int_{\sqrt{\frac{h}{Kt}}}^{\infty} F(r) dr. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In this equation the first term relates to the small particles which have

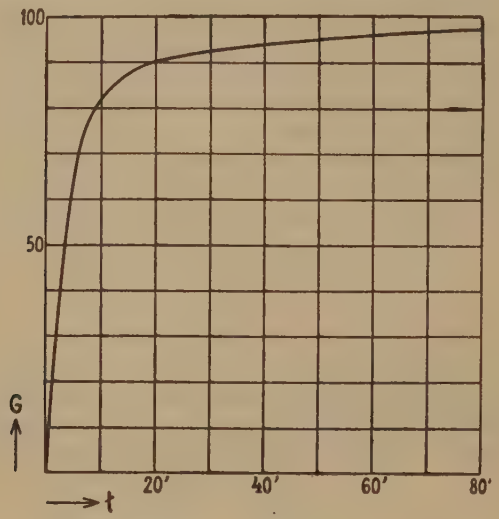

Fig. 93.—Curve of Sedimentation Velocity.

not yet settled out at time t, the second expression to the larger ones, which according to equation (4) have settled completely.

For the distribution $F(r)$ we have

$$F(r_1) = -2\sqrt{\frac{K}{t}} t^{\frac{5}{2}} \frac{d^2G(t)}{dt^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where

$$r_1 = \sqrt{\frac{h}{Kt}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If the second differential coefficient is deduced from the G, t curve found experimentally, then from (7) we get the portion $F(r_1)$ belonging to particles of radius r_1; r_1 is determined by equation (8), using the same value of t as used in equation (7). We get from the G, t curve of Fig. 93 the same curve of distribution as represented in Fig. 94. The place of greatest curvature in the G, t curve corresponds to the maximum in the distribution curve.

The fact must frequently be taken into account that the particles are not spherical as required by Stokes' law. We may then—in a similar manner as above (p. 351) for the Brownian movement of non-spherical particles—introduce spherical particles which are equivalent in their behaviour to

non-spherical particles. Instead of the true dimensions of the particles, we then use in the equation the so-called *equivalent radius*.

Nordlund [1] successfully applied Odén's method to mercury sols. He found that the distribution curves were decidedly affected by the method of preparation of the sol. With sols prepared by electrical disintegration the curve had a sharp maximum; this was flatter with a sol prepared by vaporization, and much flatter for a sol produced by shaking (cf. p. 513 concerning this method of preparation).

Odén's sedimentation method presupposes the validity of Stokes' law.

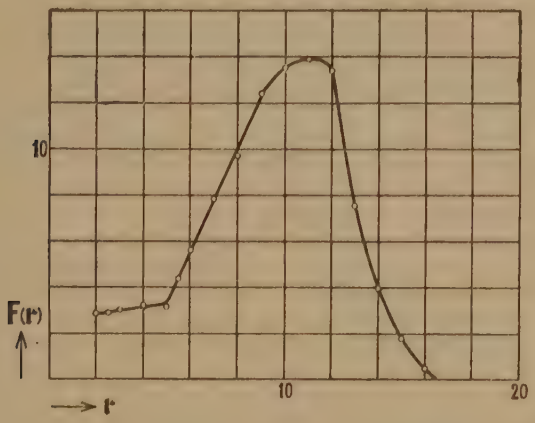

Fig. 94.—Curve of Distribution deduced from Sedimentation Velocity.

According to Nordlund's discussion and experiments [2] it is valid in liquids not only for macroscopic solid particles, but also for microscopic and submicroscopic solid and liquid particles. It is only in gases that departures from it occur (cf. p. 780). A condition which, as already remarked, must always be fulfilled (cf. p. 350) is that the particles fall at a sufficient distance from a solid wall. This is always fulfilled for macroscopic measurements; it is only with ultramicroscopic measurements that its fulfilment becomes doubtful. Westgren [3] has introduced the influence of the wall quantitatively into Stokes' formula.[4]

The Shape of Colloidal Particles

In the discussion of the light absorption by sols and the dependence of the Tyndall light upon the wave-length and its polarization, conclusions have already been drawn concerning the shape of the colloidal particles. Thus the result was arrived at that the colour of red gold sols can only arise from particles approximately spherical in shape; that is, if they are crystalline, no axis is of excessive length. On the other hand, these particles are certainly not strictly spherical, since the light scattered at an angle of

[1] "Experimentelle Studien über Quecksilberhydrosole, die aus metallischem Quecksilber hergestellt sind." Diss., Upsala (1918). Kolloidzeitschr. **26**, 121 (1920).

[2] Diss., Upsala, 1918, p. 41 *et seq.*

[3] Ann. d. Physik (4), **52**, 308 (1917).

[4] Concerning the fall of non-spherical particles see Boselli, Compt. rend. **152**, 133 (1912).

90 degrees to the direction of incidence does not consist entirely of polarized light, but also contains ordinary light. It was further shown that the blue colour of many gold sols cannot in all cases arise from the particles being larger or coagulated. Judging from the polarization of the Tyndall light, they must still be small. Their blue colour is therefore probably due to a particular shape, but it remained an open question whether their particles are rod- or disc-shaped. The same was found to be true of silver sols.

From the ultramicroscopic and macroscopic behaviour of the Tyndall light further conclusions may be drawn in a comparatively simple manner concerning the shape of the particles.[1] The following argument is, strictly speaking, only correct if the double refraction which must necessarily arise with anisotropic particles has certain properties. It must be either a *rod-double refraction*, that is, one caused exclusively by the anisotropy of the shape of the particles, not by that of the constituent molecules, and hence not an *intrinsic double refraction*; or if the particles have an intrinsic double refraction the latter must fulfil certain requirements (cf. p. 411). The argument may, however, be developed with these simplified assumptions, since they render intelligible the circumstances upon which the observed optical behaviour somehow depends. When further we speak below of *spherical* particles, we mean that the three main axes do not differ much in length; in the case of *disc-* or *leaf-shaped* particles one axis is much shorter than the other two; with *rod-shaped* ones, two axes are much shorter than the third. Now, it results from the theory of the Tyndall light for non-spherical particles, while introducing the reservations and assumptions just mentioned, that strong Tyndall light occurs with particles the long axis of which lies in the direction of the electrical vector of the laterally diffracted light, and that only weak Tyndall light arises from particles which are short in the direction of the electrical vector.[2]

Hence the shape of the particles already produces an effect under the ultramicroscope. A rod-shaped particle only gives a strong diffraction image when its length lies in the plane of observation, at right-angles to the direction of the incident light; if it is placed at right-angles to the plane of observation or parallel to the direction of the incident light, its longitudinal axis does not fall in the direction of the electrical vector, and the diffraction image becomes so weak as to be invisible. In a sol containing such particles, therefore, we see in general only particles which lie in the plane of observation with their longitudinal axes at right-angles to the direction of incidence of the light. If the particles are comparatively small and in lively movement, they show, on account of their sudden assumption of the easily visible position and their sudden departure from it, a distinct *twinkling*, which is clearly distinguishable from the steady Tyndall light due to spherical particles. If the particles are large enough and the difference between the longitudinal and lateral extension sufficient, the shape can be recognized directly from the diffraction image. These phenomena can be beautifully observed with a vanadium pentoxide sol[3] which has been kept for some time. The twinkling is already observable in sols a few months old; rod-shaped particles, which behave under the ultramicroscope in the manner described, can be observed in sols from one to several years old,

[1] *Diesselhorst* and *Freundlich*, Physik. Zeitschr. **17**, 117 (1916).

[2] See *Gans, loc. cit.* p. 385; *Diesselhorst* and *Freundlich, loc. cit.* under [1].

[3] *Diesselhorst, Freundlich* and *Leonhardt, Elster-Geitel*-Festschrift, 1915, 453. *Freundlich*, Zeitschr. f. Elektrochemie, **22**, 27 (1916); *Kruyt*, Koninkl. Akad. v. Wetensch. Amsterdam, **24**, 1664 (1916); Kolloidzeitschr. **19**, 161 (1916).

or in those which have been coarsened by coagulation with electrolytes and repeptization with a fresh quantity of the dispersion medium (cf. p. 471).

If it is desired to draw conclusions macroscopically from the nature of the Tyndall light, this cannot be done from sols at rest and unaffected by external influences. The particles must be orientated in some direction, either by a motion of the liquid or by external electric or magnetic forces. The influence of motion of the liquid may be first considered. It is evident that no difference in the Tyndall light from spherical and non-spherical particles will be observable as long as the liquid is at rest (if we leave aside differences in the state of polarization). The particles lie quite irregularly; and that a certain fraction of the particles, when non-spherical, only radiate a weak Tyndall light simply results in the light from such a sol being weaker. If, however, the liquid be set in motion by stirring, non-spherical particles are arranged in a certain direction; *on account of the friction between adjoining stream filaments moving at different velocities, rod-shaped particles set themselves with their length parallel to the stream lines, and disc-shaped ones so that the disc lies in a stream surface of equal velocity.* If then on stirring streams of various directions are set up, the particles of each single stream are similarly orientated, and send according to their position stronger or weaker Tyndall light to the observer. Streams of different direction therefore contrast in appearance. The sol shows upon stirring marked *streaks*, as may be observed, for similar reasons, in liquids which are just beginning to crystallize, and therefore contain fine crystals.[1] Such streaks are best seen when the sol is illuminated in a dark room with a powerful beam of light and stirred. It is immediately obvious that the Tyndall light from sols with spherical particles is in no way influenced by the motion of the liquid. The presence or absence of streaks therefore allows us to decide whether the particles are spherical or not. The vanadium pentoxide sol referred to above, the prototype of a sol with rod-shaped particles, shows these streaks very plainly indeed.[2]

If we are now to distinguish between rods and discs, the sol must be allowed to flow regularly through a tube of rectangular section. It is illuminated by linearly polarized light, and an experimental arrangement is used in which the outflowing liquid can be observed not only at right-angles to the broad and narrow sides of the outflow tube, but also longitudinally in the direction of flow. The three main optical directions, namely, direction of the incident light, of the electrical vector, and of observation, can be made to coincide in six different ways with the three main directions of the flow tube, namely that of liquid flow, that at right-angles to the broad side, and that at right-angles to the narrow side; and thus six different flow experiments may be made, which are set out in Fig. 95. Strictly speaking, we have only three cases, for it is only a question of the direction of the electrical vector compared with the direction of flow, while the directions of illumination and of observation can be interchanged. Use is here made of the simplification usual in the kinetic theory of gases, that we assume one-third of the particles to be in each of the three main positions; thus with rod-shaped particles one-third are parallel to the electrical vector, one-third at right angles to it, but parallel to the direction of incidence; and one-third at right angles to both electrical vector and direction of incidence.

[1] Further also in suspensions which contain leaf-shaped particles, such as many clay suspensions (cf. *Le Chatelier, van Bemmelen*-Festschrift, 1910, p. 168.

[2] *Diesselhorst* and *Freundlich, loc. cit.* p. 404.

Table 111 further shows whether brightening or darkening occurs during flow under the various conditions, and it is seen that two cases occur, in which rods and discs may be distinguished. Thus darkening occurs with rods, and brightening with discs, when the illumination is parallel to the flow, the electrical vector at right angles to the narrow side, and observation at right-angles to the broad side (Exp. 1*a*); and the same difference exists when the directions of illumination and observation are interchanged (Exp. 2*b*).

TABLE 111

Behaviour of Tyndall Light with Rod- and Disc-shaped Particles in Flow Experiments

No. of Flow Exp.	Direction of Incidence.	Electrical Vector.	Direction of Observation.	Tyndall Experiment on Rods.	Discs.	Spheres.
1*a*	∥ to flow	⊥ to narrow side	⊥ to broad side	●	○	No change
1*b*		⊥ to broad side	⊥ to narrow side	●	●	
2*a*	⊥ to broad side	∥ to flow	⊥ to narrow side	○	○	
2*b*		⊥ to narrow side	∥ to flow	●	○	
3*a*	⊥ to narrow side	⊥ to broad side	∥ to flow	●	●	
3*b*		∥ to flow	⊥ to broad side	○	○	

With rods the brightening of the Tyndall light, assuming that it occurs at all, is plainer than with discs. For at rest only one-third of the rods are

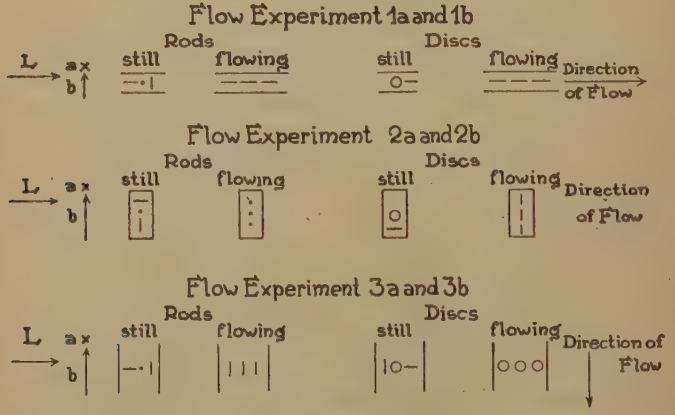

FIG. 95.

in a position in which they give a strong Tyndall light, but two-thirds of the discs are so orientated (see Fig. 95). If upon flow taking place all rods and discs come into the active position, the number of rods giving

Tyndall light is multiplied by three, while the number of active discs is only increased by one-half.[1]

All the phenomena here described were completely confirmed with the rod-shaped particles of the vanadium pentoxide sol. An arrangement suitable for this purpose is shown in Fig. 96. The flow tube F consists of two parts, which can be pressed together by rubber rings; the channel is ground into one part, so that one can observe at right-angles to both broad and narrow side. A and B are pieces of plate glass, which are separated by the plate-glass ring C; one can thus look through from above in the direction of flow.

The shape of the particles of the following sols is known with great probability, in part already from the dependence of the Tyndall light and the absorption of light upon the wave length and state of polarization. The majority were distinguished by the appearance of streaks and by the flow experiments just described.

Approximately *spherical* particles appear in

Red gold sols[2] (the state of polarization shows that the particles are not strictly spherical; X-ray spectrographic experiments (cf. p. 413) prove that the particles are crystals, probably therefore octahedra; see also Diesselhorst and Freundlich, *loc. cit.* p. 404).

Silver sols[2] (collargol; Diesselhorst and Freundlich, *loc. cit.*; here also X-ray experiments (cf. p. 413) revealed a crystalline structure).

Platinum sols (by Bredig's method, see p. 509; Diesselhorst and Freundlich, *loc. cit.* p. 404).

Arsenic trisulphide sols (Diesselhorst and Freundlich, *loc. cit.* p. 404).

Mastic sols (Diesselhorst and Freundlich, *loc. cit.* p. 404. The conclusion may also be directly drawn, from the shape of coarser droplets, which under the microscope are seen to be spherical).

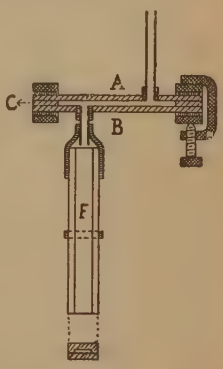

Fig. 96.

Discs or *platelets* occur in:

Old ferric hydroxide sols (probable from flow experiments. Diesselhorst and Freundlich, *loc. cit.* p. 404).

Blue gold sols with small particles (see p. 384).

Rods occur in:

Vanadium pentoxide sols (Diesselhorst and Freundlich, *loc. cit.* p. 404 and p. 408).

Tungstic acid sols (Diesselhorst and Freundlich, *loc. cit.* p. 404).

Dye sols (benzopurpurin, aniline blue, etc. Recent experiments by Zocher[3]).

[1] This is only true when the flow in the whole section of the tube is such that no liquid layers of equal velocity are present. In strips of liquid of equal velocity no orientation of the particles takes place; the increase of the number of active rods and discs is less.

[2] See also *Bergholm* and *Bjornståhl* [Physik. Zeitschr. **21**, 137 (1920)].

[3] Zeitschr. f. physik. Chemie, **98**, 293 (1921).

The Double Refraction of Lyophobic Sols

The double refraction occurring in many sols is closely connected with the non-spherical shape of colloid particles, as has already been pointed out. It is particularly strong in the case of the vanadium pentoxide sol repeatedly referred to, where it was first examined more closely.[1]

A freshly made, not too concentrated sol exhibits, whether at rest or in motion, neither double refraction nor formation of streaks (p. 404). When the sol has aged, often within some days, in any case after a few weeks, double refraction appears; at rest the sol remains dark between crossed Nicols, but upon stirring, the field of view brightens up strongly. The formation of streaks is frequently not yet visible, nor the twinkling of the particles in the ultramicroscope, when the double refraction is already quite marked. Double refraction of this kind produced by stirring the liquid we will call *stream double refraction.*

What this phenomenon depends upon becomes clear when the sol is allowed to flow through a tube of rectangular section. If it be then examined between crossed Nicols at right-angles to the direction of flow, it also remains dark during flow, if the electrical vector of the light is parallel or at right-angles to the direction of flow; a strong brightening occurs when the electrical vector is at an angle to the direction of flow, most strongly at 45°. The layer of liquid through which the sol is flowing therefore behaves like a plate of an optically uniaxial crystal cut parallel to the optic axis, with its optic axis parallel to the direction of flow. Since the elongated particles of the vanadium pentoxide sol set themselves during flow with their long axes in the direction of flow (see p. 404), the optical axis of the flowing liquid lies in the direction of their length. It is very probable that the optic axis of the single V_2O_5 particle coincides with its long axis, but this is not absolutely essential.

If we examine the flowing sol in such a manner that the directions of flow and of observation are parallel to each other, we get in convergent polarized light the well-known axial cross with the concentric rings.[2] With a quarter-wave plate of mica it may be decided whether the sol acts as a positive or negative uniaxial crystal. The behaviour was found to be positive; that is, the ordinary ray, which vibrates with its electrical vector at right-angles to the optic axis, and therefore at right-angles to the long axis of the particles, travels more rapidly than the extraordinary ray, which vibrates parallel to the long axis of the particles.

An axial cross is also obtained, as Zocher[3] observed, when the sol is allowed to rotate in a cylindrical tube between crossed Nicols with the axis of rotation in the direction of observation. The particles then lie upon concentric circles, and the cross is produced in a manner similar to the case of a spherocrystal, say a starch grain. We cannot here go into details of the spatial arrangement of the stream double refraction, to a great extent explained by Zocher; for example, the fact that the axial cross is usually rotated through a definite angle to the chief planes of polarization. From such peculiarities it will perhaps be possible to draw conclusions as to the shape and size of the particles.

The double refraction is so strong that it may be shown directly. If the sol is allowed to flow through a tube of triangular section, and this is

[1] *Diesselhorst, Freundlich* and *Leonhardt, loc. cit.* p. 404; *Freundlich, loc. cit.* p. 404.
[2] *Diesselhorst* and *Freundlich,* Physik. Zeitschr. **16,** 413 (1915).
[3] *loc. cit.* p. 407.

used as a prism for a spectral line—the red hydrogen line was used—the line is divided into two when the sol flows. These two are oppositely polarized: the more strongly refracted one, having the lower velocity, vibrates parallel to the direction of flow and to the long axis of the particles; this is the extraordinary ray, which in accordance with the positive uniaxiality is propagated the more slowly.[1]

Mechanical motion is not the only means, as already remarked, by which the particles of the vanadium pentoxide sol can be orientated and ordered. This may also be effected by means of the *electrical current* and the *magnetic field*. The rod-shaped particles will then probably set themselves in the direction of the current lines and the lines of magnetic force.

As a matter of fact this expectation is completely fulfilled by the behaviour of the sol. If the sol be examined between crossed Nicols and an electric current passed, so that the direction of observation is at right-angles to the direction of the current, the sol remains dark, when the electrical vector is at right-angles or parallel to the direction of the current; at every intermediate angle brightening occurs, most strongly at an angle of 45°. This arrangement corresponds exactly to that described above, in which the sol flows through a tube of rectangular section.

Kruyt [2] carried out similar experiments under the ultramicroscope. Originally only such particles can be seen as lie in the plane of observation and practically at right-angles to the incident light; those parallel to this direction or vertical to the plane of observation are invisible. The particles could actually be brought to disappear by making the directions of current and observation parallel to one another, and thus the long axis of the particles parallel to the direction of illumination. About two minutes after cutting off the current the original state was restored on account of Brownian movement. Conversely more particles became visible, when the current direction was vertical to the direction of observation and lay in the plane of observation; all particles were then orientated with their long axes vertical to the direction of illumination in the plane of observation. The latter experiment succeeded better with alternating than with direct current.

Bergholm and Björnståhl [3] have also proved, by means of a more refined method of observation, that red gold sols and silver sols become doubly refracting with alternating current; a further proof of the fact that the particles of these sols (at least a portion of them) are not spherical in shape but depart from sphericity in a definite manner. With gold one might soonest expect the formation of leaflets.

In the *magnetic field* the following cases were tested, and fulfilled theoretical expectations. Parallel linearly polarized light parallel to the lines of force, both therefore in the direction of the longitudinal axis of the particles, failed to give brightening at any direction of the electrical vector. Parallel linearly polarized light vertical to the lines of force and to the axes of the particles gave the same result as in the experiments just mentioned with mechanical or electrical currents; with horizontal lines of force the field remained dark with the electrical vector vertical and horizontal, and brightened with the vector in any other position, most strongly at 45°. Quantitative experiments have not yet been carried out; it may be said approximately, that with the sols hitherto investigated, a field of about

[1] *Diesselhorst* and *Freundlich*, Physik. Zeitschr. **16**, 422 (1915).
[2] *loc. cit.* p. 404.
[3] *loc. cit.* p. 407.

3,000 gauss is necessary for double refraction to be clearly exhibited. We may further remark here, that the strengthening and weakening of the Tyndall light considered on p. 405 as the result of mechanical motion must also be obtainable in a similar manner electrically and magnetically. Experiments in this direction have not yet been undertaken.

Even before these phenomena had been described in connexion with vanadium pentoxide sols, it was already known under the name of the Majorana phenomenon, that very old ferric hydroxide sols show double refraction in the magnetic field in the manner just described.[1] It was now found that this phenomenon coincides with the phenomena just described in connexion with a V_2O_5 sol. An Fe_2O_3, sol which showed the Majorana phenomenon strongly, also became doubly refracting by mechanical and electrical currents, showed streaks, and so on.[2] In the case of both sols the phenomenon is due to the presence of non-spherical particles, which can be orientated and ordered by mechanical, electrical, or magnetic means. Here also experiments are already known[3] which show how quickly the Fe_2O_3 particles set themselves under the influence of the magnetic field, and assume their original position upon its disappearance. The results are not quite definite, since for the Fe_2O_3 sol the size of the particles, which cannot be seen ultramicroscopically, is not known; the V_2O_5 sols, which can be more easily resolved optically, are more promising.

That this orientation of the particles under external influences is determined by their shape may be regarded as certain. But a further question presents itself. Does the double refraction arise from optically isotropic but non-spherical particles being arranged like a grating, or is it caused by the particles themselves being anisotropic? In other words, are we dealing with a *rod double refraction*, or with an *intrinsic double refraction*? This could be decided if we could imbed the particles in a medium of the same refractive index. Double refraction due to rods would disappear, intrinsic double refraction would remain. Such experiments have not yet been carried out, and are difficult; but the double refraction is so considerable with all these sols, that it is preferable to assume an intrinsic one. The strength of the double refraction does not necessarily run parallel with that of streak formation and with the effect of flow upon the Tyndall light. Thus with the tungstic acid sols referred to above (cf. p. 407) the formation of streaks and the variation of the Tyndall light while flowing are very strong, the double refraction comparatively weak, while with V_2O_5 and Fe_2O_3 sols the double refraction is much stronger. But the conclusion cannot be drawn that with V_2O_5 and Fe_2O_3 sols we have an intrinsic double refraction, with tungstic acid sols one due to rods, but only that with the latter the shape and size of the rods affect particularly strongly the variation of the Tyndall light, while the intrinsic double refraction is sensibly less. A small part of the double refraction is probably always due to rods.

In this section we will not go further into the question as to its amount, since no experiments are available which permit of a decision (cf. on the

[1] *Majorana*, Rend. Accad. d. Linc. **11,** I, 536, 539 (1902); **12,** I, 90, 139 (1902); *Schmauss*, Ann. d. Physik (4), **10,** 658 (1903); **12,** 186 (1903). Particularly *Cotton* and *Mouton*, Ann. de chim. et de phys. (8), **11,** 145, 289 (1907).

[2] *Diesselhorst, Freundlich* and *Leonhardt, loc. cit.* p. 404; *Freundlich, loc. cit.* p. 404. As I afterwards found, *Quincke* [Ann. d. Physik (4), **15,** 28 (1904)] and *Tieri* [Rend. Accad. d. Lincei (5), **19,** 470 (1910)] also observed the double refraction of a Fe_2O_3 sol due to motion, without, however, drawing further conclusions from it.

[3] *Corbino*, Physik. Zeitschr. **11,** 756 (1910).

other hand p. 720). Only so much may be said, that rod double refraction must always be positive, while intrinsic double refraction may be either positive or negative. If a rod-shaped colloid particle is intrinsically negatively doubly refracting, then the stream double refraction must also be negative, since the particles set themselves with their axes in the direction of the current. If, on the other hand, we are dealing with a negatively doubly refracting disc instead of a rod, the axis stands at right-angles to the surface of the disc. During flow the disc sets itself with its surface in the lines of flow, with the axis therefore at right-angles to the lines of flow. The stream double refraction of a negatively doubly refracting disc is therefore positive; conversely, that of a positive one negative.[1] This circumstance perhaps explains the curious dependence observed by Cotton and Mouton [2] of the double refraction of Fe_2O_3 sols upon the strength of the field, the size of the particles, and so on. They concluded that to explain the now positive, now negative double refraction, two kinds of particles must be assumed. These are possibly distinguished from one another by rod and disc shape.

With this description the reservations and assumptions are explained which were introduced on p. 403 in connexion with the Tyndall light and formation of streaks. With stronger intrinsic double refraction of the particles the arguments there given are only valid when rod-shaped particles are positively, disc-shaped particles negatively doubly refracting. For with positive double refraction the ray vibrating in the axis of the particle will be propagated more slowly, hence absorbed and reflected more strongly. We thus get the stronger Tyndall light, when the direction of the electric vector of the incident light is along the axis of the rods and in the direction of the stream. Disc-shaped particles, on the other hand, set themselves with their surfaces along the lines of flow, with their axes at right-angles thereto. If they are negatively doubly refracting, the ordinary ray for which the electrical vector falls in the surface will be more strongly absorbed, more strongly reflected, and will give the stronger Tyndall light.

An important question not yet settled is the influence of the size of the particles and of the distance between them upon the stream double refraction. According to Weigert [3] it only occurs at all when both the particles and the distance between them are amicronic. The close connexion between the double refraction and the age of the sols and the change in the ultramicroscopic appearance with age would then be difficult to explain.

Sols of notable double refraction are given by certain dyes, e.g. benzopurpurin and aniline blue.[4] Both sols are to a great extent hydrophobic. That of benzopurpurin results upon simple solution of the dye in water, that of aniline blue upon pouring the alcoholic solution into an excess of water. The sols of benzopurpurin show negative stream double refraction. The behaviour of aniline blue sols is peculiar. This dye has a strong absorption band in the orange-yellow and green. Upon the one side of this band, in the red, the flowing sol is negatively doubly refracting, in the blue positively. Hence in the spatial distribution of colour with stream double refraction colours appear which differ widely from those ordinarily observed.

[1] *Zocher*, Zeitschr. f. physik. Chemie, **98**, 313 (1921).
[2] *loc. cit.* p. 410.
[3] *Weigert* and *Pohle*, Kolloidzeitschr. **28**, 158 *et seq.* (1921).
[4] *Zocher, loc. cit.* p. 407.

They cannot be more fully described here. Under the ultramicroscope this sol shows rod-shaped micellæ.

Apart from the colours due to interference accompanying double refraction, the colour of many of these doubly refracting sols shows many peculiarities. This is true of the strongly coloured sols, such as those of V_2O_5 and Fe_2O_3. Thus it was found that with flowing V_2O_5 sols the ordinary and extraordinary rays are absorbed to a different extent, that therefore a *dichroism* is present, which may be called *stream dichroism*. If polarized light with vertically vibrating electrical vector was allowed to fall on the rectangular flow tube, darkening occurred with vertical flow, brightening when the electrical vector was horizontal. The extraordinary ray is therefore more strongly absorbed than the ordinary, for in the extraordinary ray the vibrations are parallel to the long axes of the particles. Since during flow all the particles are set vertically, the absorption is stronger than in the sol at rest when light with a vertical electric vector falls upon it. The absorption becomes weaker with the vector horizontal, since during the flow the third of the particles, which is to be regarded as lying horizontally when the sol is at rest, and which strongly absorbs this vector, now being vertical absorbs less strongly. This stronger absorption of the extraordinary ray agrees with Babinet's rule, according to which in absorbing doubly refracting media that ray is the more strongly absorbed which travels the more slowly, and this is the more strongly refracted extraordinary ray.

The Tyndall light always amounts to a definite fraction of the total light absorbed by the particles of the sol. Further, the circumstances favourable to a strong diffraction of the light are also as a rule favourable to absorption. It will be strong when the electrical vector is parallel to the long axis of non-spherical particles, weak when at right-angles thereto. Here again, however, the same reservation must be made as upon p. 404; either the rod double refraction must preponderate, or, if intrinsic double refraction preponderates, it must be positive for rods, negative for discs. Hence, on these assumptions, changes similar to those described above for the Tyndall light (p. 404) also occur during flow in the light absorption by sols with non-spherical particles. Brightening—strengthening of the Tyndall light—corresponds to increased absorption, a weakening of the Tyndall light to a smaller absorption. With spherical particles the absorption is naturally also independent of flow. This behaviour and the extensive parallelism to the behaviour as regards the Tyndall light was confirmed by Diesselhorst and Freundlich.[1]

Dichroism manifests itself in V_2O_5 sols not only by a strengthening or weakening of the transmitted polarized light, but also by a change in its colour.[2] When the light with vertical electric vector is darkened by flow, it also appears redder; the spectrum extends in fact from 710 to 582 $\mu\mu$, while with the sol at rest it extended to 558 $\mu\mu$. With horizontal electric vector the light appears yellower with flow, the spectrum extended to 542 $\mu\mu$.

All these circumstances, under which the light passing through the particles undergoes such considerable changes, necessarily imply that the strong double refraction also depends upon an anisotropy of the molecules which build up the non-spherical particles.

The behaviour of the V_2O_5 sols has not yet been quantitatively investi-

[1] *loc. cit.* p. 404.

[2] *Diesselhorst, Freundlich* and *Leonhardt, loc. cit.* p. 404; *Freundlich, loc. cit.* p. 404.

gated. The dependence of the double refraction of Fe_2O_3 sols upon the strength of the magnetic field and the concentration of the sol is according to Cotton and Mouton [1] very complicated, but may probably be explained in the manner suggested above (p. 411) from the different behaviour of rods and discs in stream double refraction. The fine structure of these colloid particles may possibly be elucidated by measurements of these quantitative relationships.

The State of Aggregation of the Colloid Particles of Lyophobic Sols

The phenomena described in the preceding sections show definitely that the question of the state of aggregation of colloid particles can by no means be answered simply and generally, but must be decided from case to case. The opinion was formerly general, to which I also inclined myself, that in the vast majority of sols the particles could be regarded as amorphous-solid, in the same state, therefore, as glass-like melts assume on quick cooling. The following circumstance affords a certain justification for this view. With a majority of lyophobic sols the particles come into being from a rapid abolition of a state of supersaturation, under conditions, therefore, which favour the unstable amorphous-solid state of matter rather than the crystalline.

Thus it appeared not improbable that the particles of the metallic sols might be amorphous-solid. But the optical properties of gold and silver sols already teach us that this is not the case. As already mentioned (p. 385), the particles approach the spherical form, but the state of polarization of the Tyndall light shows that they nevertheless depart from it in a definite manner, and are therefore presumably octahedral crystals. The definite proof of crystalline structure was given by the method of Debye and Scherrer (cf. p. 332). X-ray spectrograms of precipitated, coarsely crystalline gold were compared by Scherrer with those of the particles of gold sols [2]; a commercial protected sol of the firm of von Heyden, and an amicronic sol protected by gelatine (prepared by Zsigmondy) were investigated; the dry powder of the disperse phase obtained from the sols was used. In all cases line spectra were obtained, and the lines of the micellæ made from the sol lay at exactly the same points as those from the larger gold crystals. They differed only in being much broader. From the breadth of the lines the length of the edge of the gold crystals (assumed to be cubical) of the Zsigmondy gold sol was calculated from formula (2), p. 333, as 1·86 $\mu\mu$. This agrees well with the value 1·6 $\mu\mu$ which is obtained by the measurement of osmotic pressure as described upon p. 557. Also in the case of silver sols from the firm of von Heyden, Scherrer obtained the line spectrum of silver.

It is hence no longer to be doubted that the particles of these sols consist of minutest crystals, or, more correctly expressed, that in the micellæ of these sols minute crystals of the metals are contained. The behaviour of these sols generally is not in contradiction to this fact. If gold or silver sols are evaporated to dryness, or are coagulated by electrolytes, the disperse phase separates as a fine solid powder, which may unhesitatingly be regarded as finely crystalline, although no structure can be clearly made out under the microscope. Probably the case is similar with other metallic sols.

Matters are less simple with the vanadium pentoxide sol. Here the

[1] *loc. cit.* p. 410.
[2] *Zsigmondy*, "Kolloidchemie," 3rd Ed., 1920, p. 399 *et seq.*

idea naturally suggests itself that we are dealing with small rod-shaped crystals. Reinders [1] could moreover show that if with a crystalline body, such as silver chloride, the crystallization is checked by colloids such as gum (see p. 596), sols or suspensions are obtained which have properties to a large extent similar to the vanadium pentoxide sols. An experiment by Debye and Scherrer [2] showed that here also the particles from an older sol obtained by careful evaporation give an X-ray photograph with broad lines, the lines being in the same positions as those of a powder which had been obtained from melted vanadium pentoxide, after cooling to a crystalline mass. From the breadth of the lines it follows that the crystals contained in the sol are very small.

The macroscopic behaviour of the disperse phases appears surprising in view of this crystalline structure. If one coagulates a concentrated sol, which shows strong double refraction and rod-shaped diffraction images in the ultramicroscope, it sets to a jelly; more dilute sols deposit slimy, frequently wadding-like masses; upon evaporation we get horn-like masses with conchoidal fracture, or, when the amount of disperse phase is small, beautifully red, continuous translucent pellicles, which are similar to coatings of varnish. In short, these masses of vanadium pentoxide, thus separated, behave like the very prototype of an amorphous-solid body, which one would not suppose to have any crystalline properties, if the double refraction, the shape of the particles, and, decisively, the X-ray spectrogram did not teach us otherwise. How this behaviour is to be explained is an open question. Perhaps we are dealing with the crystals of a hydroxide, having the following properties. Its velocity of crystallization is very small, so that the crystals only grow very slowly. This is indeed known in the case of other crystals (cf. p. 336). Hence the actual growth of the crystals plays a smaller part than their aggregation to larger flocculi, as will be considered later (p. 416) in the case of coagulation. They thus produce, really on account of their shape, a fine network, which can envelop large masses of water; a behaviour which will also be discussed in connexion with coagulation (see p. 416). The structures containing much water, which are thus produced, bring about the appearance of amorphous separation. Possibly the further circumstance comes into play, that the space lattice of the crystals themselves can contain water molecules, as in the case of protein crystals which imbibe water (cf. p. 724).

The behaviour of old Fe_2O_3 sols is less difficult to explain, and is in accordance with expectation. Fresh sols, which show a slight double refraction, give very gelatinous flakes; on the other hand, from old sols with strong double refraction, the flakes are much more granular and more crystalline.

With the benzopurpurin sols above-mentioned we observe a behaviour which throws a strong light upon all these phenomena.[3] If the sol is produced by dissolving the dye-stuff in water and is warmed, it is perfectly clear and shows no stream double refraction—even after cooling, provided it be not too concentrated. If it be slowly coagulated, by adding to 100 c.c. of a 0·1 per cent. sol 8 to 12 c.c. of a 1-molar KCl solution, the liquid shows strong stream double refraction and gives streaks. Upon the addition of still more electrolyte the dye separates in flocculi. If these be peptized anew by washing with cold water, we again get a sol showing stream double refraction and streaks, which only loses these properties on warm-

[1] Kolloidzeitschr. **21**, 161 (1917).
[2] See *Zocher*, Zeitschr. f. physik. Chemie, **98**, 312 (1921).
[3] *Zocher*, Zeitschr. f. physik. Chemie **98**, 319 *et seq.* (1921).

ing. If, on the other hand, a clear sol prepared by warming and not doubly refracting be rapidly flocculated by pouring into an excess of the coagulating electrolyte solution, and the flocculi thus produced be peptized with water in the cold, we get without further warming a sol without double refraction or streaks.

Here we have it in our power to produce at will sols with double refraction or without. In dilute solution the micellæ of the sol prepared by warming are so small that they do not produce stream double refraction. If they are quickly coagulated, they aggregate to irregular flocculi, and these disperse again on peptization to micellæ as small as those originally present, or also to large groups of micellæ, which are however so irregularly built that they show no stream double refraction. If, on the other hand, we slowly coagulate the sol not showing double refraction, the micellæ aggregate to form larger regularly built groups, which cause stream double refraction. Such groups are preserved when the flocculi thus generated are again peptized.

With the other hydrophobic sols, especially the sulphides and selenium, we have for the present no reason to regard the particles as other than amorphous-solid. This is especially true for other hydroxide sols ; it has already been mentioned above (p. 334) that beryllium hydroxide, precipitated under similar conditions to those obtaining in the formation of a sol, is amorphous-solid in the X-ray spectrogram. It is of course not impossible that, with many of these, more exact investigation will show that the particles are extremely finely crystalline.

The Stability of Lyophobic Sols

We come to a group of particularly important and peculiar phenomena when we discuss the stability of hydrophobic sols. We are at present only concerned with aqueous sols, since only isolated data have been obtained concerning non-aqueous sols. These phenomena are important because they play a considerable part both in the arts and in the living organism ; they are peculiar, because a series of quite distinct processes are closely linked in a manner the like of which is hardly met with elsewhere. Hence it is not surprising that, in spite of the work of many years, undertaken from various points of view, many problems are still only partially solved.

It has already been remarked (cf. p. 370) that the equilibrium towards which a sol tends is the Perrin sedimentation equilibrium. The rate of fall is however so small for the minute particles that this equilibrium is not attained at all within the time during which a sol is observed. It is the peculiar property of the hydrophobic sols that small amounts of electrolyte can completely alter this state of equilibrium as well as the conditions of fall, by allowing the particles to coalesce to larger flakes, which then settle much faster. The active amounts of electrolyte are so small that traces of electrolyte present from the start, or small amounts of foreign substances dissolved from the walls of the vessels, may effect this flocculation or *coagulation*. The expressions flocculation or coagulation are regarded as equivalent in the following pages. The flocculation by electrolytes is by far the most important influence affecting the stability of the sols ; of the other influences many may be referred back to it. Hence for the present only flocculation by electrolytes will be considered.

It does not depend, as already said (cf. p. 342), upon the electrolyte altering the Brownian molecular movement directly. The colloid particles

show the same displacement after as before the addition of electrolyte, and none the less the micellæ have been altered. This shows itself as follows. Before addition of electrolyte, we observe with a permanent sol under the ultramicroscope only very rarely that two particles in contact remain together; only rarely, that they remain adhering to the walls of the observation trough. After the addition of the amount of electrolyte which suffices for flocculation, it is found to be the rule that two particles which approach each other sufficiently closely remain in contact and settle as larger flocculi, in obedience to gravity, also that they remain adhering to the wall of the trough.

Macroscopically the process manifests itself by the originally clear sol becoming cloudy immediately or some time after addition of the electrolyte; the resultant flocculi are soon large enough to be recognized directly as such. They settle on the bottom of the vessel or fill the whole liquid as a gelatinous mass. As is well known, the colour of sols depends greatly upon the size and shape of the particles (cf. p. 383). Hence a change in colour often accompanies coagulation by electrolytes, as in the case of many metallic sols. This is particularly beautiful and evident in the case of red gold sols. As soon as the single particles coalesce to form double and multiple particles, the colour of the sol becomes violet or blue; the transition is usually so quick and clear that it may be compared with the sudden change of the colour of an indicator. A similar sudden change of colour, also from red to blue, was found by Wo. Ostwald [1] with Congo-rubin sols; with some sulphide sols colour changes have also been observed.[2]

The investigation of flocculation is rendered very difficult by the fact that we have no effective and convenient method of measuring it. It is obviously a velocity process, the progressive decrease in the original number of particles. Macroscopically this is obviously difficult to follow, since the external changes during the transition of the original particles to larger flakes proceed very gradually and are comparatively slight, even when a colour change takes place, as with gold sols. Paine [3] was the first to measure a *coagulation velocity* (abbreviated C.V.), in the case of a copper sol—more correctly copper oxide sol, since oxidation certainly occurs in its preparation (cf. p. 375). He took from time to time samples of the sol to which electrolyte had been added, separated the coarser flakes by vigorous stirring and heating from the finer ones, and titrated the latter, which remained suspended in the liquid, with nitric acid; the CuO particles dissolve in the latter, especially on warming, so readily that their amount can be determined by titration to the first excess of acid. In this method the circumstance, to be discussed later, plays a part, that coarser particles are more quickly made to coalesce by stirring than fine ones (cf. p. 439).

Other cases, susceptible of macroscopic measurement, are found among the hydroxide sols, for instance, aluminium hydroxide [4] and ceric hydroxide [5] sols. Many but not all sols of this kind do not deposit flocculi, but become on coagulation uniformly more viscous, and finally gelatinous. The change

[1] Kolloidchem. Beihefte, **10,** 179 (1919).

[2] *Fr. V. v. Hahn,* Kolloidzeitschr. **27,** 172 (1920) (with selenium sulphide and silver sulphide sols).

[3] Kolloidchem. Beihefte, **4,** 24 (1912).

[4] *Miyazawa,* Journ. Chem Soc. Tokio, **33,** 1179, 1210 (1912); *Ishizaka,* Zeitschr. f. physik. Chemie, **83,** 97 (1913); *Freundlich* and *Ishizaka, ibid.* **85,** 398 (1913); *Gann,* Kolloidchem. Beihefte, **8,** 64 (1916).

[5] *Fernau* and *Pauli,* Biochem. Zeitschr. **70,** 426 (1915); Kolloidzeitschr. **20,** 20 (1917).

in the viscosity with time can be followed and we can assume that it runs parallel to the coagulation. This is certainly only so very approximately.

The final value for the viscosity which is indeed reached in the flocculation of the Al_2O_3 sol is independent of the nature of the electrolyte only in the case of a few electrolytes with inorganic kations and anions, and yet it should be universally so, if change of viscosity were proportional to coagulation.

The viscosity of a sol changes during flocculation in a rather complicated manner. Its behaviour can therefore not be interpreted until we have examined more closely the process of coagulation (cf. p. 439).

With sols such as those of gold, the colour of which changes greatly during coagulation, the course of coagulation can also be followed spectrophotometrically.[1]

By far the least open to objection is the ultramicroscopic method applied by Zsigmondy[2] and his co-workers to gold sols, and by Kruyt and van Arkel[3] to selenium sols. The number of particles in a coagulating sol is determined from time to time. Here also serious difficulties have to be overcome and disturbances taken into account: the influence of the walls and amicronic particles, and the necessity of obtaining a sufficient number of single values for each individual determination of the number of particles.

Coagulation depends in such an exquisite and special manner upon the nature of the electrolyte that at first investigators were satisfied with determining the gross differences between them, by the aid of semi-quantitative methods. This may be achieved much more easily. The complete process of flocculation was therefore not followed, but those concentrations of various electrolytes were determined which produced the same change in the sol within a given time; for instance, within five minutes the blue coloration of a gold sol, or within one or two hours the complete flocculation of a Fe_2O_3, As_2S_3, or other sol. A single point of the C.V. curve is thus determined. Electrolyte concentrations measured in this way are called *coagulation values*, or *flocculation values* (abbreviated F.V.). As we shall see later, these values have, in view of the special course of the C.V. curve, a definite, easily recognizable meaning. With reference to its function of inducing coagulation the flocculating electrolyte, or the ion which is particularly active, is called the *coagulator*.

Coagulation by electrolytes is undoubtedly the influence which everywhere primarily affects the stability. The true solubility of the particles must not, however, be neglected completely. It produces the result that the particles become larger and finally reach the limit at which the sol is no longer stable. That sols of $BaSO_4$, AgCl, etc., keep so badly in water, depends partly on the fact that these substances are already too soluble. It is quite probable[4] that the metals, oxides, etc., which so preferentially give colloidal solutions, have a far smaller solubility. Yet this influence is small compared with that of coagulation, and one continually meets with cases, e.g. of V_2O_5 sols (cf. p. 414), where the increase in size of the

[1] *Mukherjee* and *Papaconstantinou*, Journ. Chem. Soc. **117**, 1563 (1920).

[2] Nachricht. d. k. Ges. d. Wiss. Göttingen, 1907, 1; Zeitschr. f. Elektrochemie, **23**, 148 (1917); Zeitschr. f. physik. Chemie, **92**, 600 (1918); *Westgren* and *Reitstötter*, *ibid.*, **92**, 750 (1918).

[3] Chemisch. Weekblad, **16**, 220 (1919); *A. E. van Arkel*, "Uitvlokkingssnelheid van het selensol." Diss., Utrecht, 1920; *Kruyt* and *A. E. van Arkel*, Rev. d. trav. Chim. d. Pays-Bas, **39**, 656 (1920).

[4] *v. Weimarn*, Kolloidzeitschr. **4**, 130 *et seq.* (1909).

particles on keeping resembles a flocculation rather than the growth of homogeneous larger crystals.

The Dependence of Flocculation upon the Nature of the Sol and of the Electrolyte

Upon what other properties of the micellæ does the fact depend that after the addition of electrolyte they coalesce and adhere to the walls? This question may be definitely answered, if not in a perfectly general manner, at least in many limiting cases. Let us take first some possibilities that may be excluded. In the case of oil emulsions, which as regards flocculation closely resemble other hydrophobic sols, Ellis [1] showed that the range of concentration of the coagulator, in which the oil-drops quickly coagulate, stands in no relation to the interfacial tension between oil and aqueous solution. Ellis [1] and Powis [2] then determined, by means of kataphoretic experiments, the charge upon the oil-drops at various concentrations of the coagulator. The widely spread opinion, first put forward by Hardy,[3] that coagulation occurs when the particles are completely discharged, and the isoelectric point has therefore been reached, was not confirmed either. But it did result from these experiments of Powis that as soon as the electrokinetic potential ζ at the interface oil—solution, or the electric charge e, falls below a certain absolute value, coagulation takes place. This appears strikingly from Fig. 97, due to Powis. As abscissæ the cube roots of the concentrations [4] of the electrolyte $ThCl_4$ have been plotted, as ordinates for Curve 1 the potential difference ζ, for Curve 2 the degree of turbidity β. The latter is of course inversely proportional to the degree of coagulation; the smaller the turbidity, the greater the number of drops which have collected above as second phase, and the stronger the coagulation. It is seen how the emulsion becomes unstable as soon as ζ reaches the value $\mp$ 0·04 volt. We have a sharply defined flocculation zone between two non-flocculation zones. If at still higher concentrations of electrolyte the potential again assumes smaller positive values than + 0·04 volt, the stability again decreases. For oil emulsions this critical potential, which we will term the *first critical potential* (for the first critical charge corresponds to it), had approximately the same value for salts with kations of different valency; with KCl about — 0·030, for $BaCl_2$ — 0·028, for $AlCl_3$ — 0·030. Powis was able to deduce a similar behaviour from Burton's experiments (cf. p. 262) for a positive CuO sol. This sol became unstable when the kataphoretic migration velocity reached a value below $1{\cdot}4 \times 10^{-4}$ cm. per sec. for 1 volt per cm., and the potential

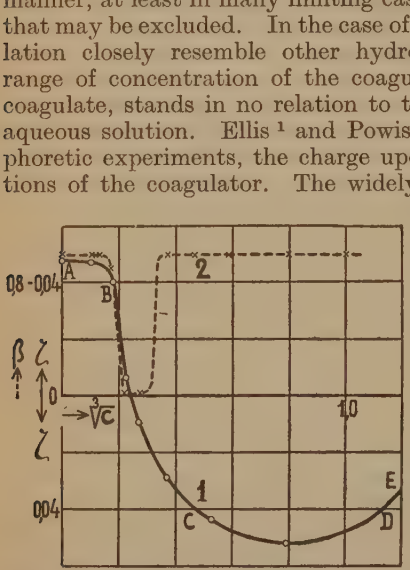

Fig. 97.—Relation between the Electrokinetic Potential ζ and the Degree of Turbidity β.

[1] Zeitschr. f. physik. Chemie, **80**, 597 (1912).
[2] Zeitschr. f. physik. Chemie, **89**, 186 (1915).
[3] Proc. Roy. Soc. London, **66**, 110 (1900).
[4] This only in order to make the drawing clearer.

ζ of the particles had fallen to about + 0·021 volt; and this was true for K_2SO_4, K_3PO_4, and K_3FeCy_6. If so low a value was not reached, the sol remained unaltered.

With this conclusion, further experiments of Powis [1] upon As_2S_3 sols did not, however, entirely agree. A first critical potential was indeed found, below which these sols became unstable. But the value was not the same for all kations. It amounted for $BaCl_2$ to — 0·026, for $AlCl_3$ to — 0·025, for $Th(NO_3)_4$ to — 0·026 in good agreement, but with univalent kations the values were quite different; with KCl the sol coagulated in a concentration of 40 millimols per litre at a potential of — 0·044 volt, with HCl at 30 millimols and a potential of — 0·05 volt. The electric charge of the particles is therefore certainly an important, but not the only circumstance, which determines coagulation. What the nature of this other influence is, remains an open question. Powis points out that the oil emulsion and the CuO sol had few particles, while the As_2S_3 sol on the other hand was comparatively concentrated; he speaks further of the salting-out effect of the potassium salt at a higher potential. I suspect that here an influence is at work which appears so strikingly in coagulation by mixtures of electrolytes (cf. p. 462) and seems to be connected with the hydration. We can therefore only state somewhat approximately that the same critical potential is reached for all electrolytes, and that then coagulation takes place. This is probably correct only with markedly electrocratic sols, among which must be reckoned the oil emulsions, probably the gold sols, and sulphur sols according to Weimarn (cf. p. 461). In the following we shall make use of the simplifying supposition, that also sols like the sulphides, the hydroxides, etc., become unstable towards all electrolytes at one and the same critical potential, although this is only true with reservations.

A change in the electrical properties of the micella is therefore a real cause of flocculation. If we neglect the details of the kinetics and only inquire what condition is necessary for a coagulation to take place at all, or for it to reach a certain degree, then this one-sided aspect of the whole range of these phenomena may be generally described as an electrokinetic one. For it is a question of the charge e being reduced by a certain amount, in order that flocculation may take place. The flocculation values are numbers in using which we content ourselves to regard coagulation only from this point of view. Hence these values are to a certain extent subject to the laws which hold for the effect of electrolytes upon electrosmosis, kataphoresis, etc., as discussed on p. 258. Flocculation has been more fully investigated in this respect than the electrokinetic phenomena proper, so that in the case of flocculation many experimental results are available which are wanting in the other cases.

In electrokinesis we have first of all the contrast between positively and negatively charged wall-layer. In accordance with this, positive and negative sols show in the fullest degree a symmetrical behaviour; the behaviour of anions in the one case corresponds to that of kations in the other.

Evidently it is the *discharging* effect of the ions (see p. 259) which is of primary importance. The discharge is always effected by the ions which carry a charge opposite to that of the particles of the sol; hence with positive sols anions have this action, with negative ones kations. The

[1] Journ. Chem. Soc. London, **109**, 734 (1916).

influence of the adsorbability [1] of the active ion and of its valency [2] again appears; the latter influence also depends upon the adsorbability. Tables 112, 113, and 114 give a clear picture of this behaviour. In them we have

TABLE 112

Flocculation Values of some Negative Hydrophobic Sols

γ (Millimol per Litre)

Electrolyte.	γ of As_2S_3 Sol [3] (1·85 g./litre).	γ of Au Sol.[4]	γ of Pt Sol [5] (0·14 g./litre).	γ of Congorubin Sol [6] (0·1 g./litre).
NaOH	—	—	130	about 390
$\frac{K_3 \text{ Citrate}}{3}$	> 240	—	—	$\frac{Na_3 \text{ Citrate}}{3}$ 525
K-acetate	110	—	—	—
K-formate	86	—	—	—
K-benzoate	—	17	—	—
LiCl	58	—	—	—
NaCl	51	24	2·5	105
KCl	49·5	—	2·2	96
KNO_3	50	25	—	102
$\frac{K_2SO_4}{2}$	65·5	23	—	102
HCl	31	5·5	—	0·23
$\frac{H_2SO_4}{2}$	30	—	0·24	0·24
$AgNO_3$	—	—	0·22	—
Aniline hydrochloride	2·5	—	—	0·37
Morphine hydrochloride	0·42	0·54	—	—
Crystal violet	0·165	—	—	—
Neufuchsin	0·11	0·002	—	—
$Ba(OH)_2$	—	—	0·058	about 4
$MgCl_2$	0·72	—	—	1·7
$MgSO_4$	0·81	—	—	0·39
$CaCl_2$	0·65	0·41	—	—
$SrCl_2$	0·635	—	—	—
$BaCl_2$	0·69	0·35	0·058	—
$ZnCl_2$	0·685	—	—	—
$UO_2(NO_3)_2$	0·64	2·8	0·065	—
$Pb(NO_3)_2$	—	—	0·011	—
Quinine sulphate	0·24	—	—	—
$AlCl_3$	0·093	—	—	0·245
$Al(NO_3)_3$	0·095	—	—	—
$\frac{Al_2(SO_4)_3}{2}$	0·096	0·009	0·013	0·03
$Ce(NO_3)_3$	0·080	0·003	—	—

[1] *Freundlich*, Kolloidzeitschr. **1**, 321 (1907); Zeitschr. f. physik. Chemie, **73**, 385 (1910).

[2] First observed by *H. Schulze* [Journ. f. prakt. Chemie, **25**, 431 (1882); **27**, 320 (1883)].

[3] These numbers from measurements by *Freundlich* are to some extent not quite free from objection, since they were obtained from sols of various concentrations and then recalculated for a reference sol, without sufficiently taking into account that the influence of the concentration of the disperse phase of a sol is not the same for coagulators of different activities (see p. 447). But the differences in concentration and the effect of the recalculation were generally not great.

[4] Prepared by reduction with formaldehyde according to *Zsigmondy's* method (cf. p. 504). Measurements by *Freundlich* and *v. Elissafoff* [Zeitschr. f. physik. Chemie, **79**, 417 (1912)].

[5] Measurements by *Freundlich* [Zeitschr. f. physik. Chemie, **44**, 152 (1903)].

[6] Measurements by *Wo. Ostwald* [Kolloidchem. Beihefte, **10**, 209 (1919)].

the F.V. (flocculation value) γ in millimols per litre, which always refers to the concentration of the coagulator after dilution by the sol. The measurements were carried out in very various ways: with As_2S_3, Pt, and Fe_2O_3 sols the coagulator concentrations were determined which flocculated completely in a given time (usually 2 hours); with Au and Congo-rubin sols the concentrations were such as produced a sudden change of colour; with Au sol in 5 minutes from red to violet; with Congo-rubin sol in one hour from red to violet. In the experiments with Al_2O_3 in Table 113, C.V. curves were measured. In the case of Gann's experiments that concentration has been taken as F.V. at which the C.V. had about the same value; in those of Ishizaka the concentrations are such as raised the initial viscosity of the sol by 10 per cent. in 30 minutes. In Table 114 there are given, along with the F.V. of a gold sol, the numbers which were already

TABLE 113

Flocculation Values of some Positive Hydrophobic Sols

γ (Millimol per Litre)

Electrolyte.	γ of Fe_2O_3 Sol[1] (0·823 g./litre).	γ of Al_2O_3 Sol according to measurements by Gann.[2]	Ishizaka.[3]
NaCl	9·25	77	43·5
KCl	9·0	80	46
NH_4Cl	—	100	43·5
$\frac{BaCl_2}{2}$	9·65	—	—
KBr	12·5	150	—
KI	16	about 300	—
KCNS	—	112	67
KNO_3	12	—	60
$\frac{Ba(NO_3)_2}{2}$	14	—	—
HCl	> 400	—	—
$\frac{Ba(OH)_2}{2}$	0·42	—	—
K-benzoate	—	13	—
K-salicylate	—	8	5·3
K-picrate	—	4	Na picrate 4·7
K-sulphanilate	—	—	95
K_2SO_4	0·205	0·28	0·30
Tl_2SO_4	0·22	—	—
$MgSO_4$	0·22	—	—
K_2CrO_4	—	0·60	0·95
$K_2Cr_2O_7$	0·195	—	0·63
K_2-oxalate	—	0·36	0·69
K_2-succinate	—	—	0·84
H_2SO_4	about 0·5	—	—
$K_3Fe(CN)_6$	—	0·10	0·080
K_3-citrate	—	0·30	—
$K_4Fe(CN)_6$	—	0·08	0·053

[1] Measurements by *Freundlich*, Zeitschr. f. physik. Chemie, **44**, 151 (1903).

[2] Kolloidchem. Beihefte, **8**, 125 (1916). The experiments relate to two slightly different sols of 0·761 and 0·651 grm. Al_2O_3 per litre.

[3] Zeitschr. f. physik. Chemie, **83**, 97 (1913). The experiments relate to a sol of 0·573 grm. Al_2O_3 per litre.

included in Table 84; they are the concentrations which produce the same depression of the potential in electrosmosis against glass. The parallelism is certainly striking.

Table 114

Comparison of Flocculation Values of Ions of Different Valency with their Influence upon the Electrokinetic Potential Difference ζ

Electrolyte.	γ of Au Sol [1] (millimol/litre).	Concentration (millimol per litre) which lowers the ζ of the Interface Glass—Water by an equal Amount.
KCl	18	25
$BaCl_2$	0·2	0·87
$AlCl_3$	0·0022	0·02
$ThCl_4$	0·0014	0·015

Also the *charging* action of ions of the same sign is readily recognized, corresponding to the initial maximum of the ζ, c curve (cf. p. 258). Small concentrations of OH′ ions raise the stability of negative sols, as was especially shown for metallic sols (p. 509). With alkalis such as NaOH coagulation only occurs at high concentrations (see Table 112). If the kation of the alkali is multivalent, as with $Ba(OH)_2$, the discharging effect of the kation greatly outweighs the charging effect of the OH′ ion. The symmetrical effect of the H˙ ion with positive sols is less clearly visible, since the latter are almost all hydroxide sols, so that a chemical action also takes place. But flocculation frequently takes place so much more quickly than the chemical reaction that one may certainly declare the F.V. of an acid to be greater than that of its salts. In the case of As_2S_3 sols alkali sulphides are, according to Mukherjee and Sen,[2] particularly effective in increasing the stability; alkali arsenites and sulpharsenites are also effective, since an alkali solution which has been saturated as far as possible with As_2S_3 makes the sol more stable; small amounts of alkali added to the sol therefore have a similar effect. These investigators therefore suppose that the large F.V. of salts with organic ions, as seen from Table 112, depends upon the increased OH′-ion concentration due to hydrolysis. The influence of H_2S upon the stability is on the other hand not clearly defined (cf. p. 465).

The *discharging* effect of oppositely charged ions is closely connected with their adsorption by the micellæ. Already in discussing the discharging action of oppositely charged ions upon the wall-layer in electrokinesis (p. 259) a close connection with adsorption was assumed. It appeared first of all in the powerful discharging action of the strongly adsorbable organic kations upon a negative wall charge. Then the special rôle of the valency could be referred to the fact that *equivalent* amounts must be adsorbed in order to produce the same discharge, but that frequently kations of different valency in *equimolecular* concentration are adsorbed to an approximately equal extent. In the case of electrokinesis this adsorption could not be directly demonstrated because the adsorbing wall-layers were hitherto too small.

[1] Prepared by reduction with CO according to *Donau* (cf. p. 505); recent measurements of *P. Scholz*.

[2] Journ. Chem. Soc. **115**, 461 (1919).

In the case of flocculation, on the other hand, the adsorption of the active ion has been successfully measured under comparable conditions, together with the F.V. or C.V. curves. This applies in particular to Gann's experiments.[1] He measured in the first place the C.V. of aluminium hydroxide sols due to various electrolytes and determined in the second place the adsorption of the active anions by ultrafiltration of the colloid particles by Zsigmondy's method and determination of the residual content of anions in the filtrate. The usual adsorption isothermal was found applicable. In addition we have the much less exact experiments of Freundlich and Schucht[2] with mercuric sulphide sols, further those of Ishizaka[3] and of Freundlich.[4] In the two latter cases the adsorption was not determined on the same colloid particles of which the flocculation was investigated, but the coagulation was compared with the adsorption on a closely related adsorbent; Ishizaka compared the coagulation of aluminium hydroxide sols with the adsorption of active ions by fibrous alumina, and Freundlich the flocculation of As_2S_3 sols with the adsorption by As_2S_3 powder, obtained from the sols by flocculation with hydrochloric acid. In all these cases the usual isothermal was found to hold, and sometimes tended clearly towards a saturation.

The fact was first of all established that equivalent adsorbed amounts belong to the flocculation values, because the same amount of discharge corresponds to equivalent amounts adsorbed, and equal discharge causes to a certain extent the same amount of flocculation.[5] Table 115 is taken from Gann's experiments.

The distinctly lower value of the amount adsorbed in the case of picrate ion depends perhaps not upon experimental error, but is possibly caused by an electrotonic action coming into play (cf. p. 294). The discharge is therefore already larger with small amounts adsorbed than in the case of less electrotonic anions.

TABLE 115

Comparison of the Amounts of Anion adsorbed by the Flocculi in the Flocculation of Al_2O_3 Sols

Anion.	F.V. millimol per litre.	Amount adsorbed at F.V. in millimol per grm. Al_2O_3.	Amount adsorbed at F.V. in Milli-equivalents per grm. Al_2O_3.
Salicylate	8	0·46	0·46
Picrate	4	0·275	0·275
Oxalate	0·36	0·275	0·55
Ferricyanide . . .	0·10	0·14	0·42
Ferrocyanide	0·08	0·11	0·44

[1] *loc. cit.* p. 416.
[2] Zeitschr. f. physik. Chemie, **85**, 641 (1913).
[3] *loc. cit.* p. 416.
[4] Zeitschr. f. physik. Chemie, **73**, 385 (1916).
[5] Whether equivalent amounts of the oppositely charged ion are really always taken up at the F.V. must still remain undecided. According to *Weiser* and *Sherrick* [Journ. Phys. Chem. **23**, 205 (1919)] and *Weiser* and *Middleton* [*ibid.* **24**, 30 (1920)], in the adsorption of anions by precipitated $BaSO_4$ and by Fe_2O_3 flocculated out of a sol, very considerable divergences from equivalence occur which cannot be referred to experimental errors. Perhaps here also the influence of hydration, which has not been sufficiently taken into account, plays a part (see p. 462).

Why the flocculation values are so extraordinarily different, although the amounts adsorbed are equivalent, is now easily understood from the course of the adsorption isothermal. Let the ions in the first instance have equal valency. In Fig. 98 the adsorption isothermals are plotted for the adsorption of salicylate and Cl′ ions by fibrous alumina (according to Ishizaka). The concentrations c in the solution, which correspond to equivalent amounts adsorbed, are obtained by drawing a horizontal straight line. These c values, which are closely connected with the flocculation values, lie widely apart, just as do the flocculation values of Table 113. It must be noted that c and γ are not the same; c is an equilibrium concentration, γ on the other hand a total concentration. The amount adsorbed a must therefore be subtracted from γ in order to get c. With weakly flocculating ions γ is so large that a may be neglected in comparison; γ and c are therefore not sensibly different. With strongly flocculating ions, on the other hand, the F.V. is sometimes so small that practically the whole ion is adsorbed. It is then by no means permissible to put $\gamma = c$. On the contrary $\gamma - a = c$.

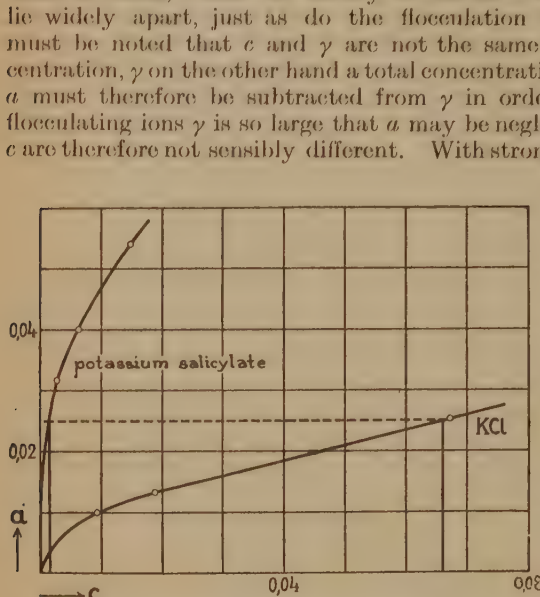

Fig. 98.—Adsorption Isothermals of Chlorine Ion and Salicylate Ion with Fibrous Alumina as Adsorbent.

Accordingly the more strongly adsorbed ion has a smaller F.V. Hence with negative sols, $H^{\cdot}$ ions, the kations of heavy metals, and organic kations have small flocculation values in accordance with their greater adsorbability. With the heavy metal kations there is further the circumstance that their adsorbability follows the electrochemical series (p. 211). For red, weakly acid gold sols Gann [1] investigated the γ values determined from the colour change to violet, of many organic compounds (amines, alkaloids, dyes, protein derivatives, etc.) and found a pronounced dependence upon the constitution. The presence of organically combined nitrogen always appeared to be of essential importance. Unfortunately, no correspondingly extensive data for the adsorption of these substances on gold (or on other adsorbents) are available which would allow of testing the expected relation between F.V. and adsorbability. With positive sols the OH′ ions and the strongly adsorbable organic anions assume a similar prominence.

The influence of valency may now likewise be referred to adsorption. In Fig. 99 the adsorption isothermals of a series of kations on arsenic trisulphide sols are plotted according to Freundlich.[2] The curves calculated in mols for the ions of various valencies $UO^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, and $Ce^{\cdot\cdot\cdot}$, do in fact lie close to one another, that for NH_4 ions only diverges slightly. Since equivalent amounts adsorbed correspond to the flocculation values, these must be to one another for uni-, bi-, and tervalent kations as $1 : \frac{1}{2} : \frac{1}{3}$. In Fig. 100 the

[1] Kolloidchem. Beihefte, **8**, 251 (1916).
[2] Zeitschr. f. physik. Chemie, **73**, 408 (1910).

adsorption curves calculated in mols for kations of various valencies are combined in a single (idealized) curve. We see how widely different are

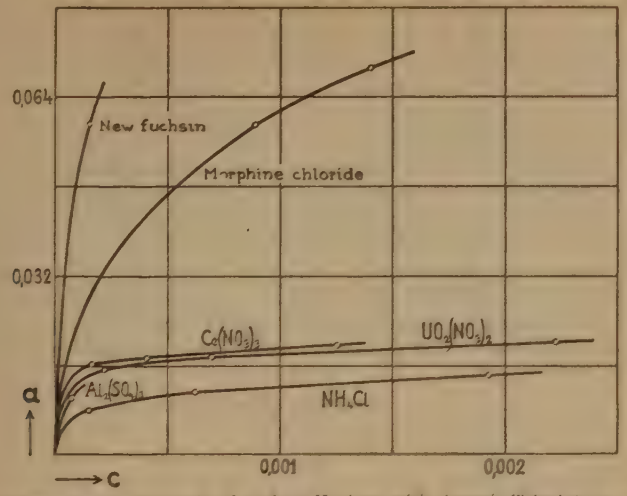

FIG. 99.—Adsorption Isothermals of various Kations with Arsenic Trisulphide as Adsorbent.

the c values, or the $(\gamma - a)$ values corresponding to them, which belong to amounts adsorbed in the ratio $1 : \frac{1}{2} : \frac{1}{3}$, and the same must then also be largely true for the γ values, as just explained. On the assumption,

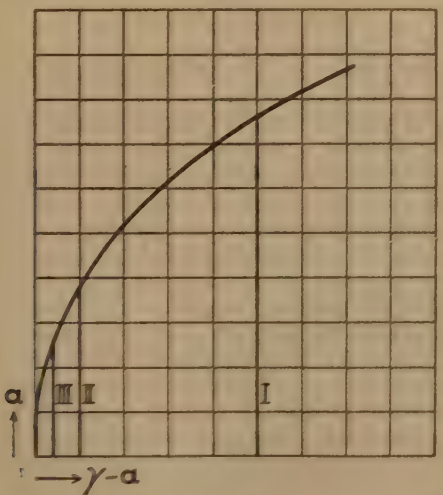

FIG. 100.—a, $(\gamma - a)$ Curve for Kations of various Valencies.

by no means accurate, of a strict coincidence of these curves, we can calculate $c = \gamma - a$ from the adsorption isothermal. In the equation

$$a = ac^{\frac{1}{n}} = a(\gamma - a)^{\frac{1}{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

we must substitute as values for uni-, bi-, and tervalent ions the numbers 1, $\frac{1}{2}$, and $\frac{1}{3}$. The graphic representation in a logarithmic diagram (Fig. 101) is only intended to show that the distances between the γ values are indeed such as the adsorption theory requires; a strict coincidence of the curves must not be concluded therefrom. The $(\gamma - a)$ values in question are those of $NH_4^{\cdot}$ ions (51 millimol per litre), $UO^{\cdot\cdot}$ ions (0·63 millimol per litre), and $Ce^{\cdot\cdot\cdot}$ ions (0·017 millimol per litre).

If ions of like valency are equally adsorbed, then their flocculation values must be approximately equal. As Tables 112 and 113 show, this holds very distinctly for inorganic anions and kations of base metals, particularly so for the bi- and tervalent kations. This fact may be applied, albeit with caution, to testing the valency of an ion. The bivalency of the beryllium ion,[1] the tervalency of the kations of the rare earths,[2] could be well confirmed by this means.

It would however amount to a complete misunderstanding of this rule (that allied ions in molar concentration are approximately equally adsorbed),[3] if it were regarded as essential to the share of adsorption in coagulation.

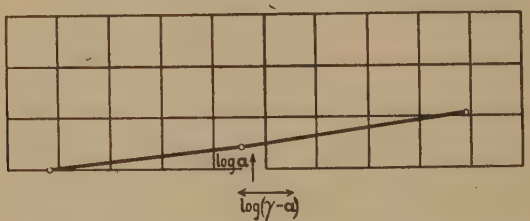

Fig. 101.—log a, log $(\gamma - a)$ Curve for Kations of various Valencies in the Coagulation of As_2S_3 Sol.

That the flocculation values of ions of the same valency cluster closely around a certain concentration, or, in the case of ions of different valency, lie apart in the manner shown in Fig. 101, and that the adsorption isothermals of the ions then coincide to a great extent, is good confirmation of the theory. But the confirmation is not less good when the flocculation values of ions of the same valency are quite different, as in Fig. 98, and when further the flocculation values of ions of different valencies lie apart in a different manner from that assumed in Fig. 101, presupposing, of course, that the adsorption isothermals diverge in a similar manner from coincidence. Indeed, no contradictory case has come to light, such as of a strongly adsorbed ion coagulating weakly, or a weakly adsorbed one strongly. Sufficient cases have, however, been observed in which adsorption isothermals do not coincide, or flocculation values differ greatly, cases where one would have expected on other grounds a certain similarity. This is true, for example, for the equivalent kations of the alkali metals with negative sols. In Table 112 it is unmistakable that the flocculation values of the ions of the alkali metals arrange themselves in the lyotropic series

$$Li > Na > K > NH_4.$$

[1] *Freundlich*, Zeitschr. f. physik. Chemie, **44**, 135–136 (1903); *Galecki*, Zeitschr. f. Elektrochemie, **14**, 767 (1908).

[2] *Freundlich* and *Schucht*, Zeitschr. f. physik. Chemie, **80**, 564 (1912).

[3] See *Wo. Ostwald*, Kolloidzeitschr. **26**, 28 and 69 (1920).

With many negative hydroxide sols this is even more striking. Thus the F.V. ranges for negative V_2O_5 sol from 130 millimol per litre for LiCl to 7·7 for RbCl.[1] Whether here the parallelism between adsorbability and lyotropic series makes itself felt (cf. p. 203), or whether the hydration of the ions asserts itself in a way not hitherto considered by theory, remains undecided. I am almost inclined to believe the latter alternative; to begin with, the sols just mentioned are much more hydrophilic than the metallic and sulphide sols, where this influence of the lyotropic series is much less pronounced. Further it could be proved[2] that with a sol of soluble S_λ sulphur (prepared, according to v. Weimarn,[3] by pouring an alcoholic sulphur solution into water) which is much more hydrophobic than a sulphur sol prepared by Odén's method (cf. p. 617), the flocculation values of the alkali metal kations differ very little, whilst with the more hydrophilic Odén sol the lyotropic series was quite distinct; thus the F.V. for the Weimarn sol ranged from 34 millimol for LiCl to 30 for CsCl, for the Odén sol between 750 millimol for LiCl and 95 for CsCl.

With various inorganic ions, especially anions, great divergence from the coincidence of the adsorption curves also occurs.[4] The divergence is almost always such that the ion of higher valency, calculated molarly, is much more strongly adsorbed than would correspond to coincidence of the curves; that is to say, the flocculation values of ions of different valencies lie further apart than in Fig. 101. This is especially striking for the adsorption of $Fe(CN)_6''''$ ions by the particles of Al_2O_3 sols (Gann). Coagulation proceeds, in agreement with this divergence, at very small concentrations.

Adsorption by the micellæ is a pronounced exchange adsorption (cf. p. 204). Anions and kations of the coagulator are therefore not adsorbed in equivalent amounts; the amount of active ion adsorbed greatly preponderates. In its place the corresponding ion of the active electrolyte, previously adsorbed on the micella, passes into solution. With As_2S_3 sols the ion which passes by exchange into the solution is the $H^\cdot$ ion, as already shown by Linder and Picton,[5] and then by Whitney and Ober[6]; with Fe_2O_3 sols it is the Cl' ion.[7]

Experiments by Fajans and v. Beckerath[8] show how much this exchange adsorption depends upon the charge of the particles. Micellæ of silver halide sols, prepared according to Lottermoser (cf. p. 372), when positively charged by adsorption of $Ag^\cdot$ ions, do not sensibly adsorb Thorium B; when negatively charged in presence of excess of halogen ion, they adsorb ThB, and the amount adsorbed moreover increases with the concentration of the halogen ions, therefore with the strength of the charge.

Pauli and Matula[9] have followed the exchange of the Cl' ion for other coagulating ions by measuring the potential. It was found that after

[1] *Freundlich* and *Leonhardt*, Kolloidchem. Beihefte, **7**, 195 (1915); the same was true of a Mo_2O_5 sol [*ibid.* **7**, 179 (1915)].

[2] Researches by *P. Scholz*, not yet published.

[3] *v. Weimarn* and *Malyschew*, Kolloidzeitschr. **8**, 216 (1911).

[4] Particularly in the adsorption of anions by fibrous alumina (from Al amalgam) (cf. *Ishizaka, loc. cit.* p. 416), and by the particles of an Al_2O_3 sol (*Gann, loc. cit.* p. 416).

[5] Journ. Chem. Soc. **67**, 63 (1895).

[6] Zeitschr. f. physik. Chemie, **39**, 630 (1902); see also *Freundlich* and *W. Neumann, loc. cit.* p. 205.

[7] *Linder* and *Picton*, Journ. Chem Soc. **87**, 1908 (1905).

[8] Zeitschr. f. physik. Chemie, **97**, 478 (1921).

[9] *loc. cit.* p. 372.

coagulation practically the whole Cl′ content of the sol was found in the solution. In the coagulation with SO_4'' ions the amount of the latter was equivalent to the quantity of Cl′ ions displaced, as Duclaux [1] had already found; that is, the SO_4'' ion is practically completely adsorbed. With univalent anions, like the NO_3' ion, the quantity required for coagulation is much greater than the amount of Cl′ ion displaced. Such experiments, carried further, would unquestionably contribute to an understanding of flocculation. On the other hand, the Fe_2O_3 sol is not the most favourable example, since in its case hydration influences make the phenomena more complicated than in the case of other hydrophobic sols.

It is perhaps not superfluous to point out that in this exchange the final state does not simply differ from the original by a new ion taking the place of the old one. On the contrary, the electrical equilibrium of the micella has been displaced in such a way as to make ζ smaller. ζ may also be made smaller by increasing the concentration in the solution of that ion which, while otherwise contained in the active electrolyte of the micella, goes into solution when exchange takes place. Acids are able to flocculate As_2S_3 sols, chlorides Fe_2O_3 sols.

It has already been mentioned (cf. p. 418) that microscopically resolvable oil emulsions are entirely similar as regards coagulation to hydrophobic sols; it may again be emphasized how completely similar is the sedimentation of the particles of a coarse suspension. Thus Bodländer [2] investigated kaolin suspensions by weighing the amount of kaolin present after definite intervals of time in a layer of a certain height. He found a great acceleration of the settlement by electrolytes,[3] an unmistakable influence of the valency of the kations, a strikingly powerful effect of the H· ion and of an organic kation (quinine hydrochloride), a depression of the rate of settling by OH′ ions, all therefore in agreement with the negative charge of the kaolin. Mastic emulsions, already frequently referred to, also follow completely the above flocculation rules. L. Michaelis, Pincussohn and Rona [4] also examined in this case whether an adsorption of the coagulating kation can be detected. The adsorption could only be demonstrated for the heavy metal kations, not for those of the light. This need not contradict the theory. Firstly, we do not know which ion is actually exchanged as mobile kation, and secondly the reversal of adsorption to be discussed later (p. 453) may result in a kation at first adsorbed being later returned to the solution so that its adsorption is difficult to demonstrate.

Reversal of Charge by Electrolytes. The Irregular Series

From Fig. 97 it may be seen that, when the active ion reverses the charge on the drops of the oil emulsion to a potential which is greater than the first critical potential, the emulsion again becomes stable; the drops are then of course charged oppositely. This reversal is likewise a very general phenomenon, shown by hydrophobic sols, and called, rather unsuitably,

[1] Journ. de Chim. Phys. **5**, 29 (1907).

[2] Nachr. d. Gött. Ges. d. Wiss. 1893, p. 267.

[3] That electrolytes hasten the settlement of suspended particles was already observed long ago. One of the oldest statements is that of *Sidell* in the year 1837 to 1838 [quoted from *Weule*, Ann. d. Hydrogr. **24**, 402 (1910)] that particles which were suspended in the water of the Mississippi, settled after addition of salts in some hours, whereas they otherwise needed days.

[4] Biochem. Zeitschr. **6**, 1 (1907).

the phenomenon of the *irregular series* by the first observers, U. Friedemann and Neisser [1] and Bechhold.[2] It appears with strongly adsorbable multivalent ions, which are easily able to reverse the charge of a wall-layer. As example we have in Table 116 the flocculation of a Pt sol by $FeCl_3$ over a great range of concentration.

In Fig. 102 this behaviour is shown graphically. AB corresponds to the

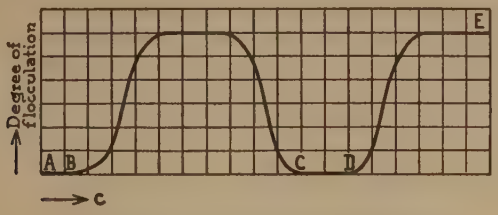

Fig. 102.—Curve of an Irregular Series.

lower non-flocculation zone, BC the lower flocculation zone, CD the upper non-flocculation zone, DE the upper flocculation zone. The same letters indicate on Curve 1, Fig. 97, the regions whose charge approximately corresponds to these zones.[3]

Table 116

Irregular Series in the Coagulation of Pt Sol by $FeCl_3$ [4]

Concentration of the $FeCl_3$ Solution (millimol per litre).	State of Flocculation.	Direction of Kataphoretic Migration.
0·0208	No flocculation	Migrates to *anode*
0·0417	,, ,,	
0·0557	,, ,,	
0·0833	Complete flocculation	Does not migrate
0·1633	,, ,,	
0·2222	,, ,,	
0·3333	No flocculation	Migrates to *kathode*
0·5567	,, ,,	
0·8333	,, ,,	
1·633	,, ,,	
3·333	,, ,,	
6·667	,, ,,	
16·33	Complete flocculation	
33·33	,, ,,	
83·33	,, ,,	
163·3	,, ,,	
333·3	,, ,,	
666·7	,, ,,	

[1] Münch. Med. Wochenschr. **51**, No. 11 (1903).

[2] Zeitschr. f. physik. Chemie, **48**, 385 (1904); extensive series of experiments by *Buxton* and *Teague*, Zeitschr. f. physik. Chemie, **57**, 64, 76 (1907).

[3] It should be noted that the degree of flocculation in Fig. 102 and the degree of turbidity on the curve of Fig. 97 have opposite meanings; the *more turbid* the oil emulsion in Fig. 97, the *less* is it coagulated, while the degree of flocculation of the (originally clear) sol is the *greater* the *more turbid* it is.

[4] *Buxton* and *Teague*, Zeitschr. f. physik. Chemie, **57**, 72 and 79 (1904).

These irregular series were first found so distinctly with the salts of tervalent metals giving difficultly soluble amorphous hydroxides, that the opinion was frequently held—also by myself—that these hydroxides enveloped the colloid particles, and so caused the reversal of charge and the flocculation phenomena. But this explanation is inadequate, for in the case of Fe_2O_3 sols irregular series have been observed for flocculation by NaOH and Na_2HPO_4,[1] in which case in the upper non-flocculating zone the charge of the sol is negative, having been reversed by the adsorption of OH' ions or PO_4''' ions. Powis [2] could readily obtain a negative Fe_2O_3 sol (with a $\zeta = -0{\cdot}036$ volt) by allowing a $FeCl_3$ solution to flow into an excess of a NaOH solution (conc. 5 millimol per litre). The NaOH solution must not be added to the $FeCl_3$ solution, for then coagulation always occurs. If he added the negative Fe_2O_3 sol to an excess of $FeCl_3$ solution (conc. 7·5 millimol per litre) he got a positive Fe_2O_3 sol with $\zeta = +0{\cdot}05$ volt. Here it is impossible to assume the formation of special enveloping substances. Hence we must admit that Kruyt [3] and Powis [4] are right in saying that the simple reversal of charge by the adsorption of the oppositely charged ion suffices as an explanation. Powis inclines towards the very probable assumption that the positive charge of the hydroxide sols is always to be ascribed to kations of high valency.

As a consequence of the irregular series *two* flocculation values must be distinguished: a lower one, applying to the original sol; an upper one, applying to the reversed sol. The first corresponds more or less to the point B in Fig. 102, the second to point D. If a sol be flocculated with a little-known coagulator, it is important to be sure that the lower F.V. is really determined and not the upper F.V. occurring at a higher concentration.[5]

It cannot be doubted that a reversed sol in the upper non-flocculating zone entirely corresponds to another sol, which has from the start the same charge. Its flocculation in this zone is determined by the oppositely charged ions, their adsorbability and valency. Extensive series of experiments on this point are not available, but a few measurements by Neisser and U. Friedemann [6] show it unmistakably. They produced in the case of a mastic sol an irregular series, firstly with $FeCl_3$, and secondly with $Al_2(SO_4)_3$. With $FeCl_3$ the upper F.V. was about 60 millimols per litre, with $Al_2(SO_4)_3$, on the other hand, 1·7 millimols. This corresponds to the great difference in the F.V. of Cl' and SO_4'' ions for positive sols (see Table 113). The extent of the region CD of Curve 1 in Fig. 97, the concentration, therefore, at which the first critical potential is reached from below, thus depends upon the nature of that ion which has a charge of the same sign as the original sol.

It is sometimes possible to distinguish clearly the reversal of charge caused by ions from the action which is produced by an oppositely charged hydroxide.[7] A neutral gold sol (prepared by reduction with H_2O_2) gave with $Th(NO_3)_4$ a characteristic irregular series as just described. In the

[1] *Kruyt* and *van der Spek*, Kolloidzeitschr. **25**, 17 (1919); further *Kruyt*, *ibid.* **22**, 81 (1919), and K. Akad. v. Wetensch. Amsterdam, **23**, 252, 260 (1914).

[2] Journ. Chem. Soc. **107**, 818 (1915).

[3] *loc. cit.* under [1].

[4] Zeitschr. f. physik. Chemie, **89**, 91 (1915).

[5] See an example of this kind in the coagulation of As_2S_3 sol by strychnine nitrate [*Freundlich*, Zeitschr. f. physik. Chemie, **73**, 402 (1910)].

[6] *loc. cit.* p. 429.

[7] *Kruyt* and Miss *Adriani*, Koninkl. Akad. v. Wetensch. Amsterdam, **27**, 658 (1918).

flocculating zones the sol became blue, in the non-flocculating zones it remained red. But if the gold sol was made feebly alkaline by NaOH the behaviour was decidedly different: in the lower flocculation zone, which lay at much higher $Th(NO_3)_4$ concentration, the flocculi were red, not blue. The individual Au micellæ united with colloidal ThO_2 were discharged, as takes place with oppositely charged sols (cf. p. 478), and were thus coagulated. As a matter of fact red flocculi of this kind are also formed when the Au sol is allowed to react with a ThO_2 sol (according to A. Müller [1]). An upper red non-flocculation zone is observed, when the ThO_2 is in suitable excess, and finally an upper flocculation zone with a blue colour; the auriferous ThO_2 micellæ are coagulated by the NO_3 ion and unite to coarser flakes, whereby the gold particles are also brought so close together that the blue colour appears.

The Kinetics of Rapid Coagulation

The two previous sections mainly deal with those sets of flocculation phenomena which may be referred to electrokinesis and adsorption, without suffering the reproach of too great or too artificial simplification. But the question: How does the coagulation depend upon the concentration of an electrolyte? already compels us to consider the actual velocity of coagulation (C.V.).

It was found first of all that with increasing electrolyte concentration the C.V. approaches a limiting value, independent of the electrolyte concentration. Zsigmondy [2] discovered this by experiments of the following kind. Under constant conditions of volume and stirring, he added to a gold sol solutions of an electrolyte, each time in greater concentration. He determined the time required for the colour to change to violet.

Table 117 shows that from a concentration of 20 millimol NaCl per litre, referred to the total volume, up to one of 500 millimols, the change takes place in about 7 secs.

Table 117

Dependence of the Coagulation Time of a Gold Sol upon the Concentration of Coagulator

Concentration of NaCl Solution (millimol per litre).	Coagulation Time.
5	Purple in 2·5 minutes.
10	12 seconds
20	7·2 ,,
50	7 ,,
75	6·5 ,,
100	7 ,,
150	6 ,,
200	6–7 ,,
300	7·5 ,,
500	7 ,,

The same was found for all other electrolytes investigated, and the important fact became evident that the constant maximum C.V., or what

[1] Kolloidzeitschr. **2**, Supplementheft I., p. VI (1907).
[2] Nachr. d. K. Ges. d. Wissensch. Göttingen, 1917, p. 1.

is the same thing, the minimum time of coagulation, is to a great extent independent of the nature of the electrolyte. Thus the coagulation time with NaCl, $CaCl_2$, $Al(NO_3)_3$, $Th(NO_3)_4$ as coagulators amounted to 5 to 7 secs. A similar dependence of the coagulation time upon electrolyte concentration was found by Lüers [1] with Congo-rubin red. At very high concentrations a fresh increase in coagulation time occurred, which perhaps depends upon the reversal in charge of the particles.

We must therefore differentiate the range of concentration of the *rapid constant C.V.* from that of the *slow variable C.V.* It is very probable that the boundary between the two regions, or more correctly, the comparatively quick transition from one to the other, is again connected with electrical properties of the micellæ. Zsigmondy assumed, no doubt correctly, that in the region of rapid C.V. the micellæ are completely or almost completely discharged, that they are there indeed near the isoelectric point. As long as the micellæ still carry as high charges as in the stable sol, they do not cohere, since the enveloping electrical double layer protects them strongly. This is not to be understood in the sense that the charge of the micella may simply be regarded as free, and that the absence of aggregation depends as a matter of course upon the repulsion due to the charges. But since the double layer is diffuse, a small part of the charge will take effect as free, especially when upon the approach of two particles the symmetrical arrangement of the double layer is disturbed, and this small free charge produces a repulsion.

It is important that this can be directly demonstrated. Perrin [2] and Costantin [3] could show with concentrated gamboge emulsions that as regards the distribution of the particles according to the hypsometric formula (see p. 343) they do not strictly obey van 't Hoff's laws, but that between the particles a repulsion exists, each particle being surrounded by a sphere of repulsion which amounted to about 1·7 times its radius.

Now as soon as the micellæ are discharged, this repulsion ceases, and they stick together, assuming that they have approached sufficiently near. As cause of this cohesion Zsigmondy assumes a special attractive force which would no doubt be similar to that acting in crystallization, and hence depend upon residual valency. We must already emphasize here what will be discussed more fully later (cf. p. 472), that in coagulation at first only coherence, but no complete fusion, of the particles takes place; the individual particles are present in the coagulum and recognizable as such.

If we consider in this connexion the ζ, c curve (see Fig. 97), we now have to distinguish two critical potentials; the already discussed *first critical potential*, which must be attained in order that flocculation may be definitely started; and further the *second critical potential* immediately at the zero of ζ, at which the slow C.V. passes into the rapid.

A theory of the rapid coagulation velocity, based by v. Smoluchowski [4] on these views of Zsigmondy, leads us to expect the following relationships. Round each discharged particle is a sphere of attraction of radius r. If two particles approach, during molecular motion, so closely that the centre of the one enters the sphere of attraction of the other, they would remain adherent and not separate again. Below the second critical potential, that

[1] Kolloidzeitschr. **27**, 123 (1920).
[2] Compt. rend. **158**, 1168 (1914).
[3] Compt. rend. **158**, 1171 (1914); Ann. de physique (9), **3**, 101 (1915).
[4] Physik. Zeitschr. **17**, 557, 583 (1916); Zeitschr. f. physik. Chemie, **92**, 129 (1917).

is, at complete discharge, in the region of the rapid C.V. every contact would be effective and hence lead to adherence.

Between the first and second critical potential not all contacts are effective, but only a certain fraction dependent upon the charge on the particles; this is the region of slow coagulation. In the following we will at first only consider rapid coagulation. The minimum value that the radius r of the sphere of attraction can have is obviously twice the radius of the particle, for then the two particles just touch; $\mathrm{r} = 2r$. Such a double particle can take up a further single particle in the same way, or also another double particle; a triple particle can do the same, and so on. v. Smoluchowski first calculates the decrease in the number of single particles which in consequence of Brownian movement diffuse into the sphere of attraction of a stationary particle, and extends the result to a large number of particles, which are in molecular motion. Then he calculates in a similar manner the decrease in the number of double and triple particles, and so on; here we must take into account that their number at first increases since they arise from the union of single particles. Hence their velocity curve shows a maximum, as in ordinary chemical kinetics, or like the velocity curves of substances which appear as intermediate products in radioactive decay and disappear again. The velocity of decrease in the number of the multiple particles cannot be calculated so rigorously as for single particles, since both the diffusion constant and the radius of the sphere of attraction can only be estimated approximately in the former case. Here the assumption is made that r is not much greater than $2r$.

It now follows from these calculations that the decrease with time of all particles takes place according to a reaction equation of the second order.

$$k = 4\pi \mathrm{Dr} = \frac{1}{t}\left(\frac{1}{\Sigma v} - \frac{1}{v_0}\right) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here v_0 is the original number of single particles, Σv the number of all particles present at a given moment, D the diffusion constant, k the velocity constant. Following v. Smoluchowski, it is instructive to solve this equation for Σv, the number of particles present at a given moment. We then get the following equations:

$$\Sigma v = \frac{v_0}{1 + kv_0 t} = \frac{v_0}{1 + \frac{t}{\theta}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$v_1 = \frac{v_0}{(1 + kv_0 t)^2} = \frac{v_0}{\left(1 + \frac{t}{\theta}\right)^2}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$v_2 = v_0 \frac{kv_0 t}{(1 + kv_0 t)^3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$v_n = v_0 \frac{(kv_0 t)^{n-1}}{(1 + kv_0 t)^{n+1}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

v_1 is the number of single particles present at a given moment, v_2 that of double, v_3 of triple, v_n of the multiple particles made up of n single ones. The equation

$$kv_0 = 4\pi \mathrm{Dr} v_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

has, as a consideration of dimensions shows, the value of a reciprocal time; it is the *specific coagulation time.*

$$\theta = \frac{1}{kv_0} = \frac{1}{4\pi \mathrm{D} r v_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The formulæ include completely at a given temperature the dependence of rapid coagulation upon the number of the particles, of course also for various concentrations of the sol. It follows from them that the time necessary for a given transformation is inversely proportional to the initial content. If we therefore have a sol with a small v_0, its "rapid coagulation" may take a long time. Hence the range of concentration of rapid coagulation is only that in which coagulation takes place with a definite maximal velocity. The time required for coagulation is therefore not necessarily brief.

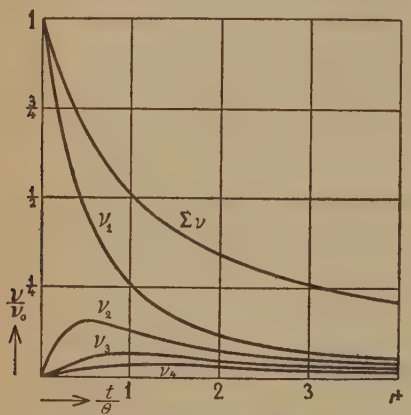

FIG. 103.—Alteration with Time of the Number of Particles.

Fig. 103 gives a graphical representation of the change with time in the numbers of all classes of particles. As abscissæ we have the relative times $\frac{t}{\theta}$, as ordinates the relative numbers of particles $\frac{v}{v_0}$.

The extent of the numerical agreement between theory and experiment is shown in Table 118, which relates to the coagulation of a gold sol, in which the diminution in the number of single particles was followed ultramicroscopically. We see that $\frac{r}{r}$ does not depart widely from 2. As was assumed at the outset, it is necessary for the coherence of the particles that they should directly touch one another. Westgren and Reitstötter [1] found good agreement with Smoluchowski's formula in the rapid coagulation of coarse gold sols; Kruyt and A. E. van Arkel [2] in that of selenium sols.

TABLE 118

Velocity of Rapid Coagulation of a Gold Sol (NaCl as Coagulator)

$v_0 = 0{\cdot}552 \cdot 10^{10}$; $r = 24{\cdot}2\,\mu\mu$; $\frac{r}{r} = 3{\cdot}12$; $k = 0{\cdot}02315$.

t (in seconds).	v (obs.) (relative value).	v (calc.).
0	1·97	1·97
2	1·35	1·65
5	1·19	1·31
10	0·89	0·93
20	0·52	0·54
40	0·29	0·25

[1] Zeitschr. f. physik. Chemie, **92**, 750 (1918).

[2] *loc. cit.* p. 417.

It is theoretically noteworthy that we have here a process which in certain respects resembles a chemical reaction velocity, for which however the velocity may actually be calculated upon the assumption that every encounter, which leads to contact, is also effective. As we know, this does not usually hold for chemical reaction velocity; if every encounter were there effective, we would observe much greater velocities than actually occur. Hence only a small fraction of encounters can be effective, and we are as yet without any simple, generally applicable conception, which allows us to say in any given case how large this fraction is, and how it is connected with the constants of the reacting substances.

The Kinetics of Slow Coagulation

Slow coagulation proceeds in a manner theoretically much more complicated. It however deserves particular attention, since it obtains in the majority of natural and technical experimental conditions.

Slow coagulation takes place between the first and second critical potential, in a range of concentration of the coagulator which causes a lowering of the potential of the micellæ below the original, in a range, therefore, in which they are partially, but not completely, discharged; we are still at some distance from the isoelectric point. This is just the range of concentration in which the flocculation value is usually determined. As was already mentioned on p. 416, the methods by which the C.V. of slow coagulation has been measured are subject to important objections.

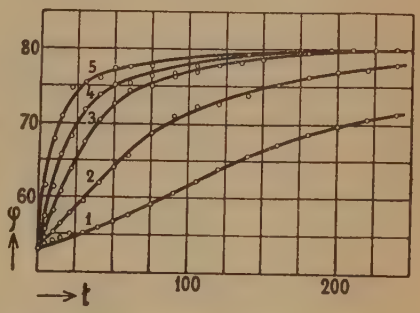

Fig. 104.—Coagulation Velocity Curves of an Al_2O_3 Sol at various Concentrations of the Coagulator.

If we consider the rate of slow coagulation without any theoretical assumption whatever, it is unmistakable that with most coagulators and under ordinary conditions of experiment it has an *autocatalytic* character: the coagulation-time curve is therefore S-shaped. During the first period after the addition of electrolyte the alterations in the sol are slight; then, after some time, the amount flocculated increases rapidly, and finally it slowly approaches the end state. In Fig. 104 the C.V. curves for the coagulation of an Al_2O_3 sol by KCl from measurements by Gann [1] are represented; the times of outflow measured with an Ostwald viscosimeter are plotted as ordinates; the times which have elapsed since the addition of the electrolyte are the abscissæ. Curve 1 relates to a KCl concentration of 60 millimols per litre, Curve 2 to one of 70, Curve 3 to one of 80, Curve 4 to one of 90, Curve 5 to one of 100 millimols per litre. As already mentioned, the increase of viscosity of the coagulating sol was followed, on the assumption that it went parallel to the degree of coagulation. A simple proportionality between increase in viscosity and content of coagulated particles certainly does not exist; the increase in viscosity is the more rapid. If in the following the curves of increase in viscosity are nevertheless regarded as C.V. curves, this is only done with caution because at the present time we are

[1] *loc. cit.* p. 416.

without any extensive experiments, involving a large number of electrolytes, and employing better methods, especially that of ultramicroscopic counting. For the same reason the following formulæ are only given because they allow the evaluation of a numerical measure for the C.V.

For the mathematical representation of the increase in the viscosity with time a differential equation

$$\frac{dx}{dt} = \varkappa(1 + bx)(1 - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

was used, which integrated gives

$$\varkappa = \frac{1}{t(1 + b)} \log \frac{1 + bx}{1 - x}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here x is the relative increase in coagulation measured by the increase in the time of efflux φ, which, as we have said, was measured by the Ostwald viscosimeter; t is the time, b and $\varkappa$ are constants, of which b may be deduced from the ordinates of the point of inflexion. How far equation (2) suffices is seen from Table 119.

TABLE 119

Rate of Increase in Viscosity of an Al_2O_3 Sol upon Coagulation by KCl

Content of Sol, 0·651 g. Al_2O_3 per litre. Coagulator Concentration, 60 millimol per litre. $b = 2{\cdot}73$; $t = 25°$

t (in min.).	ϕ (in secs.).	x.	κ.
0	52·4	—	—
2	52·4	—	—
5	52·4	—	—
10	52·4	—	—
15	52·6	0·0172	—
22	52·8	0·0345	—
30	53·0	0·0517	(0·0017)
40	53·3	0·0776	(0·0018)
50	53·7	0·1120	0·0021
60	54·1	0·1465	0·0022
75	54·5	0·1810	0·0021
90	55·1	0·2328	0·0023
105	55·6	0·2758	0·0023
120	56·2	0·3275	0·0023
140	57·0	0·3966	0·0024
160	57·8	0·4655	0·0024
	$\varphi_\infty = 64{\cdot}0$		

The constant $\varkappa$ may be regarded as a measure of the C.V.

In the experiments of Paine, which were carried out in quite a different manner (see p. 416), the reaction also had an autocatalytic character.

It is extremely doubtful whether this peculiar course of the velocity of slow coagulation is intrinsic, or is only simulated by the occurrence of accessory processes. v. Smoluchowski [1] believes that the autocatalytic course of the C.V. is *not* intrinsic. His reasons are the following. It is

[1] *loc. cit.* p. 432.

natural to assume that slow coagulation is distinguished from rapid by the fact that in the former case not all encounters between micellæ are effective, but only a proportion, which depends upon the electrolyte concentration. The process then proceeds just as with rapid coagulation, only the same relative change in the number of particles occurs after a correspondingly longer time ; we must therefore multiply the specific time of coagulation θ with a suitable numerical coefficient, or the constant k (see p. 433) with the reciprocal value of this numerical coefficient. We therefore have for the constant k' of slow coagulation

$$k' = 8\pi \mathrm{Dr}\xi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which ξ is the fraction by which k must be multiplied. The factor 2 must be introduced since every effective encounter causes two particles to disappear. We can therefore, assuming the correctness of this theory, pass from a C.V. curve of rapid coagulation to one of slow coagulation at a given electrolyte concentration by multiplying the abscissæ—the times—by a certain numerical factor ; *the curves of coagulation velocity must be affine to one another.*

No measurements are as yet available in which rapid and slow coagulation have been followed on the same sol, so that it cannot yet be definitely determined whether the curves are affine or not. But we may already anticipate here by saying that the C.V. curves of slow coagulation are indeed affine to one another. This was already found by Paine,[1] and Ishizaka [2] and Gann [3] were able to confirm it. If the C.V. curves for rapid and slow coagulation were affine, as required by Smoluchowski's theory, the autocatalytic course ought to be by no means peculiar to slow coagulation ; but the C.V. curve of rapid coagulation shows no point of inflexion.

Smoluchowski has therefore to refer the actually observed autocatalytic type to some other cause. In the case of Paine's experiments he ascribes it to the coagulated particles being separated from the not yet coagulated single ones by stirring, and to the theoretically much greater influence of stirring upon larger particles than upon smaller ones. This is an important fact, which deserves close consideration. v. Smoluchowski [4] estimates this influence as follows. Let a particle with the radius of the sphere of attraction r be at rest in the origin of the system of co-ordinates. In consequence of stirring, which is not supposed to lead to violent eddies, but only to a flow according to the laws of moderately agitated liquids, a stream of the liquid is considered to flow past the particle in a direction parallel to the x axis with a gradient towards the z axis. Let the gradient of velocity be $\frac{du}{dz}$. The velocity at a distance z between z and $z + dz$ is then $z \cdot \frac{du}{dz}$. The region of the flow with this velocity which falls within the sphere of attraction—on one side of the particle—is $2\sqrt{\mathrm{r}^2 - z^2}\, dz$ (see Fig. 105) ; the number of particles which in this region come into the sphere of attraction per second is equal to the number of particles contained in this region $\nu \cdot 2\sqrt{\mathrm{r}^2 - z^2}.dz$

[1] *loc. cit.* p. 416.
[2] *loc. cit.* p. 416.
[3] *loc. cit.* p. 416.
[4] Zeitschr. f. physik. Chemie, **92**, 155 *et seq.* (1917).

multiplied by their velocity $z\frac{du}{dz}$, hence

$$2\nu z\sqrt{r^2 - z^2}\, dz\frac{du}{dz};$$

ν is the number of particles contained in one cubic centimetre. The total number of particles which in consequence of stirring arrive per second in the whole sphere of attraction is

$$n = 4\nu\frac{du}{dz}\int_0^r z\sqrt{r^2 - z^2}\, dz = 4\nu\frac{du}{dz}r^3\int_0^{\frac{\pi}{2}} \cos^2\varphi \sin\varphi d\varphi = \frac{4}{3}\nu r^3\frac{du}{dz}. \quad (4)$$

Now according to Smoluchowski the number of particles which reach a particle in one second as a result of the Brownian movement is

$$\mathrm{n} = 8\pi\nu \mathrm{D}r.$$

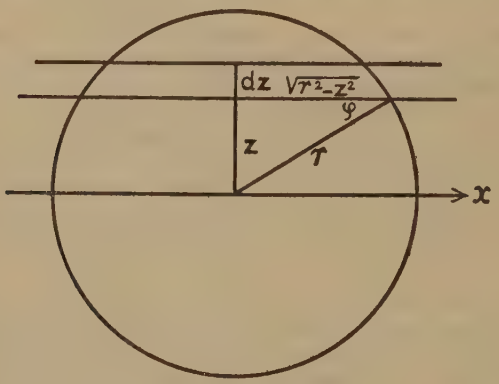

Fig. 105.

Hence the ratio of the particles which enter the sphere of attraction on account of stirring to those which arrive of their own account is

$$\beta = \frac{n}{\mathrm{n}} = \frac{r^2\frac{du}{dz}}{6\pi \mathrm{D}}.$$

If we remember that according to equation (8), p. 350,

$$\mathrm{D} = \frac{\mathrm{RT}}{\mathrm{N}}\cdot\frac{1}{6\pi\eta\nu},$$

and that $\mathrm{r} = 2r$, where r is the radius of the particles (see p. 434) we get

$$\beta = \frac{4\eta r^3 \mathrm{N}\frac{du}{dz}}{\mathrm{RT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

β therefore depends in the highest degree upon the size of the particles; with a velocity gradient $\frac{du}{dz} = 1$ we get for submicrons of radius $r = 24\,\mu\mu$ a β of about 10^{-5}, for microns of radius $r = 1\,\mu$, β becomes $= 1$. While

stirring has an extremely small effect on coagulation in the case of amicrons and submicrons, its influence becomes very considerable with larger particles.

In Paine's experiments therefore an autocatalytic course might easily be simulated by the stirring; at the beginning of flocculation the already coagulated but still small particles are not separated, while this takes place in a high degree as soon as the particles have in course of time become considerably larger.[1]

In the flocculation of sols our attention is again and again directed to this influence of stirring, especially with sulphide and hydroxide sols. It is for example noticeable that in the flocculation of arsenic trisulphide sols the sol remains unaltered in appearance even for some minutes after addition of the coagulator, nor does it show any change on stirring. After a considerable time—30 to 60 minutes—the sol is apparently still unchanged. A single stirring, even a slight vibration, then frequently suffices to fill the whole liquid with large flakes; the particles which have meanwhile grown larger by coagulation have reached the range of size in which their coalescence is greatly favoured by stirring.

Other circumstances must be considered when coagulation is followed by means of the increase in viscosity, as has been done with some hydroxide sols (cf. p. 416). We must here discuss the changes which the viscosity of a sol undergoes on coagulation. On general grounds we should expect a decrease of viscosity: for since the particles are discharged by addition of the coagulator, the increased viscosity, which was present in the original sol on account of the charge on the particles, disappears. For according to v. Smoluchowski we have in the original sol a viscosity which may be represented by the equation (cf. p. 369)

$$\eta_S = \eta_M\left\{1 + 2{\cdot}5\varphi\left[1 + \frac{1}{\lambda\eta_M r^2}\left(\frac{D\zeta}{2\pi}\right)^2\right]\right\}.$$

On the addition of electrolyte the specific conductivity λ increases, and the potential ζ of the particles decreases. The expression $\frac{1}{\lambda\eta_M r^2}\left(\frac{D\zeta}{2\pi}\right)^2$ may be neglected as compared with 1, and we have the lower viscosity

$$\eta_S = \eta_M(1 + 2{\cdot}5\varphi).$$

Since the discharge of the particles usually takes place quickly, this is also true of the decrease in viscosity. Fernau and Pauli [2] were able to show that with CeO_2 sols, in which the total coagulation is characterized by a strong increase in viscosity, a rapid decrease in viscosity at first follows the addition of NaCl. Whether the slow decrease in viscosity, which Woudstra [3] observed during the coagulation of silver sols prepared according to F. Wöhler and Muthmann's method (cf. p. 508), is to be referred to the same cause, remains doubtful, but is not impossible.

The great increase in viscosity, by means of which the coagulation of the hydroxide sols mentioned on p. 416 was studied, is due to quite different

[1] A case in which upon similar grounds the separation of a substance at first colloidally dispersed is greatly accelerated by stirring, is furnished by the separation of hydrated alumina according to *Bayer's* method. (See *Schupp*, "Studien zum *Bayer*schen Verfahren der Herstellung von Tonerdehydrat." Diss., Darmstadt, 1915.)

[2] Kolloidzeitschr. **20**, 20 (1917).

[3] Zeitschr. f. physik. Chemie, **63**, 619 (1908); also *van Bemmelen*-Festschrift, 1910, p. 36.

causes. One might at first suppose that this behaviour contradicts Einstein's theory of the viscosity of suspensions (see p. 369), since according to this theory the viscosity depends solely upon the total volume of the particles, and not upon their size. But the total volume of the particles increases greatly during this gelatinization of the sol. We may imagine with Smoluchowski [1] that the particles, which at the outset already contained much water, retain a still greater amount of the dispersion medium when they cohere. Fig. 106 indicates how the water envelope may increase when two particles unite. We must regard the liquid included within the dotted line as rigidly attached to the particles, and we then understand the increase in volume thus caused. The amount of water will obviously become still greater if a still larger number of particles unite, and if they are for instance rod-shaped and not spherical. As we see, it is only with fairly hydrophilic sols that we may count on an increase in viscosity, and it is only with them that it has been actually observed.

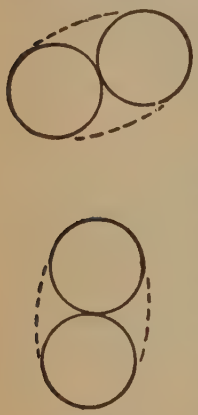

Fig. 106.

Now, as Smoluchowski remarks, this mass of water rigidly attached to the multiple particles and the increase in volume caused by it may produce the appearance of an autocatalytic course. The larger the particles become, the larger is also the amount of water which they enclose, and the larger their effective volume. While two particles which cohere bind something like the amount of water represented in Fig. 106, this amount is considerably greater for four particles, even with closest possible packing, and the amount of enclosed water increases with the number of particles in the coagulated complex. Hence at first, as long as only double particles are formed from single ones, the viscosity will increase only slowly, and then faster and faster, as soon as the flocculi contain four and more micellæ. This, however, implies an autocatalytic course.

In spite of these weighty objections to an intrinsic autocatalytic course of slow coagulation, and although the influences discussed above are certainly largely responsible for the S-shaped course of the C.V. curve, I do not wish to regard it as completely settled that the velocity of slow coagulation may not retain under certain conditions an inherently autocatalytic character of its own. Even without stirring, or following the change in viscosity, but when observing macroscopically the change in the turbidity, the colour, etc., we get the impression of an autocatalytic process. Some time after the addition of the coagulator the change is scarcely visible, and then it occurs suddenly and increases rapidly. This is, for example, very striking in the coagulation of tungstic acid sols investigated by Lottermoser [2] by means of the turbidity. The translucency of the sol was followed by means of a photo-electric potassium cell. The possibility exists, however, that, as in the case of the increase in viscosity, the larger flakes appearing in the later stages of flocculation exert a stronger influence upon the appearance than the double and triple particles at first formed.

[1] Kolloidzeitschr. **18**, 190 (1916); Zeitschr. f. physik. Chemie, **92**, 157 *et seq.* (1918).
[2] Kolloidzeitschr. **15**, 145 (1914).

Particular value must be attributed to counting experiments under the ultramicroscope. Here measurements by Westgren [1] of coarse gold sols show no autocatalytic course ; the observed C.V. curves lie, however, fairly near to rapid coagulation. Wiegner [2] and Galecki [3] believed, on the other hand, that in their observations on the flocculation of gold sols small particles had the tendency to attach themselves to larger ones, hence that the larger particles acted as coagulation nuclei. If this is really the case, an autocatalytic course would follow, for since in the first stages the larger particles increase in number, they should cause an accelerated course after some time. The ultramicroscopic experiments of Kruyt and A. E. van Arkel [4] on selenium sols also gave in some series a possible indication of an autocatalytic course. Perhaps this effect can only be observed in a pronounced form in concentrated sols, and not in dilute such as are used in the counting method under the ultramicroscope, because sufficiently large multiple particles only arise in concentrated sols. In any case Smoluchowski [5] also reckons with the possibility that such particles coagulate more strongly because their sphere of attraction is comparatively larger.

Perhaps macroscopic experiments with coarse suspensions contribute no less to the elucidation of this subject. Odén,[6] using the method described on p. 401, investigated the sedimentation of kaolin suspensions and of $BaSO_4$ suspensions peptized with citric acid, at various concentrations of the electrolytes used for accelerating sedimentation. Fig. 107 shows the sedimentation curves of a $BaSO_4$ suspension at various concentrations of the coagulator (NH_4NO_3) and equal content of disperse phase. The ordinates are the weights of the settled $BaSO_4$ in per cent., the abscissæ the times in seconds. The suspension was so uniform and so stable, that without coagulator it settled very slowly according to a linear curve marked "without NH_4NO_3." In the presence of the coagulator the curves have an autocatalytic character, which has here, however, an easily recognizable cause. Under the influence of the coagulator the original primary particles form coarser flakes, and only when the time up to their formation, the *aggregation time* of Odén, has elapsed, do the particles settle more quickly, and further they have become coarser so uniformly that the piece BC of the curve is straight, as it should be according to Stokes' law for particles of constant size. The dotted straight lines in Fig. 107 indicate at their inter-

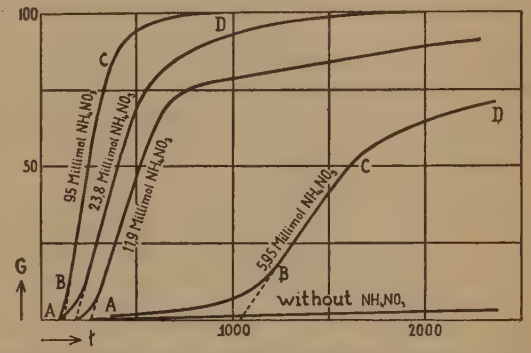

FIG. 107.—Curves of the Sedimentation Velocity of a $BaSO_4$ Suspension at different Concentrations of the Coagulator.

[1] Ark. f. Kemi, Mineral. och Geol. **7**, No. 6 (1918).
[2] Kolloidzeitschr. **8**, 227 (1911).
[3] Zeitschr. f. anorg. Chemie, **74**, 174 (1912).
[4] *A. E. van Arkel*, Diss., p. 49 *et seq.* ; *loc. cit.* p. 417.
[5] Zeitschr. f. physik. Chemie, **92**, 153 (1917).
[6] Kolloidzeitschr. **26**, 160 (1920) ; Ark. f. Kemi, Mineral. och Geol. **7**, No. 26 (1920).

section with the axis of abscissæ the values of the aggregation time. The last piece of the curve CD corresponds to the circumstance that the rest of the particles, which have not become appreciably coarser, settle more slowly.

The great similarity of these curves with those in which coagulation takes place without sedimentation suggests the following. With such autocatalytic curves we are really only dealing with coagulation proper in the first part before the upward bend which corresponds in Fig. 107 to the aggregation time. With the rapid rise some kind of secondary effect then makes itself partially felt, which is perhaps specially distinct, when the amount of disperse phase in the sol is particularly large.

The Velocity of Slow Coagulation in its Dependence upon the Concentration of the Coagulator

As remarked on p. 436, the constant $\varkappa$ may serve as a measure of the C.V., if we are able to express the C.V. curve by means of a suitable equation. But even if this is impossible, a quantity can still be given, which permits the C.V. to be measured in its dependence upon the concentration, for the C.V. curves are affine. We can therefore pass, for example, from the times of the C.V. curve observed for electrolyte concentration 1 to that for electrolyte concentration 2 by multiplying by a certain number. The reciprocal of this number, the *factor of coagulation velocity* k, is proportional to the C.V. Under ordinary conditions k is further always proportional to $\varkappa$, for both are proportional to reciprocal times for a given amount of transformation.

The extreme dependence of slow coagulation upon the concentration of the coagulator is very striking, and practically unexampled among the influences of concentration upon kinetic processes. As is evident from Table 120, in the case there chosen from Gann's investigations,[1] the velocity increased thirteen-fold when the electrolyte concentration only increased about 67 per cent. In another case, also investigated by Gann,[1] viz. that of the velocity of coagulation of an Al_2O_3 sol by potassium benzoate, the velocity increased thirty-fold (from $\varkappa = 0{\cdot}00075$ to $\varkappa = 0{\cdot}024$), while the coagulator concentration increased 60 per cent. (from 9·634 to 14·62 millimol). The results of Paine and of A. E. van Arkel confirm this extremely rapid increase with the concentration of the coagulator. This relation between coagulator concentration and C.V. could be approximately represented by putting $\varkappa$ proportional to a high power (the second to seventh) of the concentration

$$\varkappa = \text{Const.} \times c^{\nu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

a relation which cannot really be correct, since at high electrolyte concentrations the constant velocity of rapid coagulation is reached.

The following explanation of this influence of the concentration is not improbable.[2] In the range of slow coagulation the particles have a higher charge than in that of rapid coagulation. We may first assume that the attraction between the particles and the size of the sphere of attraction remain unaltered; but on account of the repulsion caused by the electric charge (see p. 432) only such particles have their spheres of attraction sufficiently close as can collide with sufficient force. Hence only those

[1] *loc. cit.* p. 416.
[2] *Freundlich*, Kolloidzeitschr. **23**, 163 (1918).

collisions are non-elastic and lead to cohesion of the particles where the kinetic energy exceeds a certain critical value. For the sake of simplicity let the sol contain, to begin with, only particles of uniform size, so that cohesion depends upon a certain critical velocity being exceeded. The velocities of the particles of a sol are distributed according to a Maxwell distribution curve (see Fig. 108) in which the abscissæ are the velocities, the ordinates the probability W, that a particle has a velocity lying between c and $c + dc$. Below the second critical potential in the neighbourhood of the iso-electric point, in the region of rapid coagulation therefore, all encounters of the particles are non-elastic at any velocity, if only the spheres of attraction have approached sufficiently closely. Since the number of particles, the velocities of which lie within a certain range, is proportional to the area between the two ordinates which correspond to the limits of the range of velocity, in the region of rapid coagulation all particles, corresponding to the total area enclosed within the curve of Fig. 108, will be capable of coagulation.

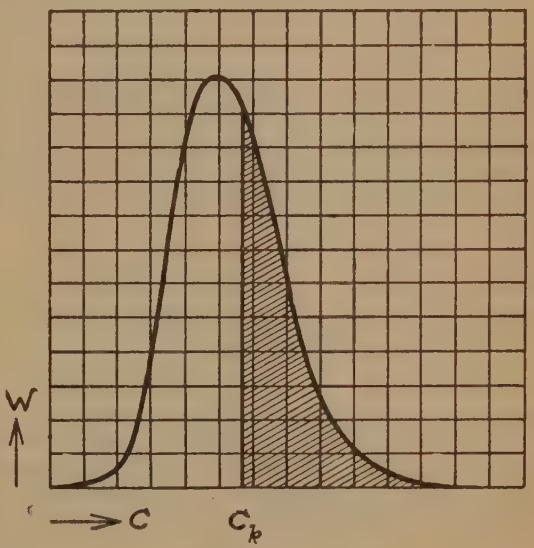

Fig. 108.—W, c Curve.

In the region of slow coagulation between the first and second critical potentials, the particles are charged, and only those particles having a velocity equal to or greater than a critical value c_k become capable of coagulation. This number of particles hence no longer corresponds to the total area enclosed by the curve, but to one limited on the left by the ordinate c_k. The number of active particles will therefore decrease but slowly at first, as long as the great majority of particles whose velocity corresponds to the mean may still be regarded as active. The decrease only becomes considerable when c_k lies on the other side of the peak, as represented in Fig. 108. Hence we have a rapid decrease in the number of particles, and connected with this a rapid decrease in the C.V., when, with decrease in the concentration of the coagulator, the charge on the particles and with it the critical velocity c_k increases.

The number of particles with a velocity between c and $c + dc$ is

$$dn = k_1 c^2 e^{-c^2} dc \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here k_1 is a constant. The total number of particles Σn, which have a critical velocity of c_k and above, is

$$\Sigma n = \int_{c_k}^{\infty} k_1 c^2 e^{-c^2} dc = k_2 \left[c_k e^{-c_k^2} + \frac{1}{2}\sqrt{\pi} - \int_0^{c_k} e^{-c^2} dc \right] \quad . \quad . \quad (2)$$

The velocity constant $\varkappa$ of slow coagulation may be put approximately proportional to the number of active particles Σn. Hence we have

$$\varkappa = \lambda_2\left[\mathfrak{c}_k e^{-\mathfrak{c}_k^2} + \frac{1}{2}\sqrt{\pi} - \int_0^{\mathfrak{c}_k} e^{-\mathfrak{c}^2} d\mathfrak{c}\right], \quad . \quad . \quad . \quad . \quad (3)$$

where λ_2 is a new constant.

The connexion between the critical velocity $\mathfrak{c}_k$ and the charge $\mathfrak{e}$ of the particles still remains to be discussed. If we neglect the possibility that the charge is irregularly distributed on the micella, and that it might make some difference whether at an encounter they are exactly opposite each other or not, we may put $\mathfrak{c}_k$ proportional to the charge $\mathfrak{e}$. For in order that the kinetic energy may overcome the repulsion we must have

$$\frac{m\mathfrak{c}_k^2}{2} > \frac{\mathfrak{e}^2}{y} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where y is the mean distance at which repulsion must be considered. The charge $\mathfrak{e}$ may be put proportional to the potential ζ of the double layer, and since in the range of concentration which is particularly concerned in coagulation, the decrease in ζ[1] with the concentration c of the active ion may be regarded as a logarithmic function of c (see p. 262), this also applies to $\mathfrak{e}$. We may therefore write

$$\mathfrak{e} = \mathfrak{k}_3 \log \frac{\gamma}{c}.$$

Hence, since $\mathfrak{e}$ is proportional to $\mathfrak{c}_k$ according to equation (4),

$$\mathfrak{c}_k = \lambda_1 \log \frac{\gamma}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $\mathfrak{k}_3$, γ, and λ_1 are further constants.

First of all we recognize that equations (3) and (5) correctly reproduce the limiting cases of the C.V. At the iso-electric point $\mathfrak{c}_k = 0$: for even a collision at the lowest velocity must be non-elastic. The first and third terms in the bracket in equation (3) become zero, and

$$\varkappa_r = \frac{1}{2}\lambda_2\sqrt{\pi} = \text{Const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

that is, we have the constant velocity $\varkappa_r$ of rapid coagulation.

For very small values of the coagulator concentration c, and hence for very large ones of $\mathfrak{c}_k$, the first term in the bracket of equation (3) becomes zero; for the third we have

$$\int_0^{\infty} e^{-\mathfrak{c}^2} d\mathfrak{c} = \frac{1}{2}\sqrt{\pi}.$$

Hence the whole bracket and with it $\varkappa_0$ becomes $= 0$. Towards small concentrations of the coagulator sols have unlimited stability, apart from other influences.

In order to test whether the rapid rise of $\varkappa$ with the concentration of the coagulator agrees with that required by equation (3), measurements by Gann [1] of the C.V. of Al_2O_3 sols may be utilized. With electrolytes with univalent and particularly with inorganic univalent ions, the viscosity

[1] *loc. cit.* p. 416.

reached in the final state is largely independent of the nature of the coagulator. The course of the viscosity may therefore to some extent be considered parallel to that of the coagulation (see p. 417). If we use values of γ and λ_1, found by trial, the dependence of $\varkappa$ upon c may be calculated within the limits of experimental error. As an example the following table may be given.

TABLE 120

Dependence of Coagulation Velocity on the Concentration of the Coagulator

Coagulation of an Al_2O_3 sol (0·651 g. Al_2O_3 per l.) by KCl
$\gamma = 200$; $\lambda_1 = 1·737$; $\lambda_2 = 0·07714$; $t = 25°$.

c (millimol per l.).	$\varkappa$ (observed).	$\varkappa$ (calculated).
60	0·0023	0·0022
70	0·0049	0·0057
80	0·011	0·0011
100	0·031	0·028

The connexion of Σn (and hence $\varkappa$) with c_k is easily seen when Σn is plotted as ordinate against c_k as abscissa, as has been done in Fig. 109. This is a so-called *pointed arch* curve, such as plays a part in the theory of heredity. We see that for $c_k = 0$ and small values of c_k the velocity is constant; we have the region of rapid coagulation with comparatively large electrolyte concentrations. Next we see the rapid decline of the velocity in the region of slow coagulation with larger charges on the micellæ, greater c_k and smaller electrolyte concentration, and finally zero velocity, as soon as the concentration of the coagulator is below a certain *threshold value*.

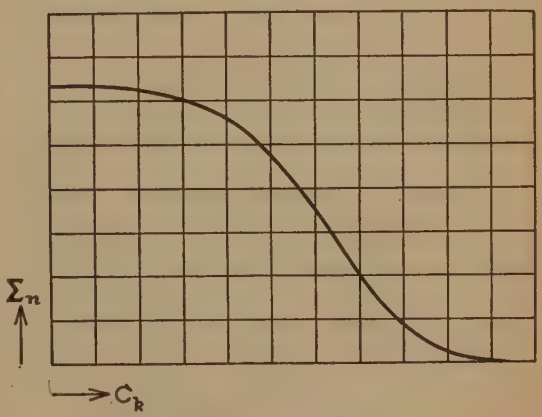

FIG. 109.—Σ_n, c_k Curve.

The existence of a threshold value of the coagulator concentration was already observed by Bodländer [1] in his investigation on the influence of electrolytes upon the sedimentation of kaolin suspensions. Its appearance is quite intelligible. The velocity sinks extremely rapidly with decrease of electrolyte concentration. Thus we get for the example in Table 120 for $c = 60$ millimols per litre and $\varkappa = 0·023$ half the total transformation in 2 hours; for $c = 30$ millimols $\varkappa$ works out at 5×10^{-6}, or half-transformation

[1] *loc. cit.* p. 428. *Spring* [Bull. d. l'Acad. Roy. d. Belg. (3), **38**, 483 (1900)] could also demonstrate a threshold value for mastic emulsions, and *Freundlich* (*loc. cit.* p. 420) for As_2S_3 sols.

in 40 days; for $c = 20$ millimols per litre $\varkappa = 3 \times 10^{-8}$, and we have a half-transformation in 15 years. As soon as a quantity changes very rapidly compared with another, a sharp transition, a threshold value, necessarily appears, as was already explained in connexion with the rate of formation of nuclei (p. 321).

It may be remarked in this connexion that very small concentrations of electrolyte may actually increase the stability, for the ζ, c curves show a maximum (cf. p. 258); that is, quite small concentrations may produce above the first critical potential a further charging of the micellæ, and thus increase the stability of the sol.

The meaning of the flocculation value also becomes intelligible from the C.V. curves. If this curve itself has been measured, as in the case of the Al_2O_3 sol, we may take as flocculation values F.V. for various electrolytes those coagulator concentrations for which the constant $\varkappa$ has the same value. The F.V. ordinarily chosen when the course of coagulation cannot be followed over a period of time (thus e.g. with As_2S_3 complete flocculation in 2 hours) is simply a comparison of concentrations for a definitely chosen C.V. curve, in which the final state is reached in 2 hours. That this can be done with some degree of precision of course depends again upon the rapid rise of the C.V. with the electrolyte concentration. For coagulator concentrations which are only slightly smaller, complete flocculation already requires a disproportionately longer time than 2 hours; with a slightly larger concentration we get the rapid coagulation which with sufficiently concentrated sols leads to the end state in a few minutes.

The sedimentation experiments of Odén mentioned above (p. 441) readily fall into line with these deductions. In the first place, the aggregation time, the time up to the linear ascent in the BC part of the curve (Fig. 107), is simply a time in which a coagulation occurs. These times are, however, not strictly comparable, since the end states are different; the flakes formed are of different sizes, as shown by the difference in the angles with which the straight parts BC rise. From the rate of fall prevailing along this part of the curve the size of the particles may be calculated by Stokes' law; it must, however, be noted that the conditions of this law—complete rigidity and sphericity of the particles—are not fulfilled, so that an equivalent radius is found, which may be different from the true one (cf. p. 403). The calculation shows a large increase in size of particles with increase of coagulator concentration, as the following table

TABLE 121

Dependence of the Size of Flakes upon the Concentration of the Coagulator in the Sedimentation of a $BaSO_4$ Suspension

Concentration of the Coagulator NH_4NO_3 (millimol per l.).	Aggregation Time.	Equivalent Radius of the largest Flakes in μ.	Number of Primary Particles in the Flakes.
5·95	17′ 20″	1	54
11·9	6′ 16″	6	11,700
23·8	3′ 10″	7	18,500
47·5	2′ 5″	8	27,600
95	2′ 0″	11	72,000
190	1′ 14″	13	118,000

by Odén for the settlement of a $BaSO_4$ suspension shows. The content of $BaSO_4$ was constant (2·78 g. per l.), the radius of the original particles, the primary particles, 262 $\mu\mu$. Although the two are not strictly comparable, the rapid diminution of the aggregation time with the coagulator concentration resembles the rapid increase, already discussed, of the coagulation velocity with the coagulator concentration. This was also particularly clear in measurements by Odén of a kaolin suspension. Below 12 millimols K_2SO_4 per litre the aggregation time was infinite. At 14·8 millimols it amounted to 365 minutes, at 98·1 millimols to 5 min. 20 secs.

Now it is highly probable that the difference in the size of the particles is quite generally a decisive factor in coagulation. In favour of this we have the following experimental facts. In the coagulation of Al_2O_3 sols the final viscosity attained depends very largely upon the nature and often also upon the concentration of the coagulator, which is quite intelligible if we are dealing with flakes of different size and composition. Frequently, e.g. in the case of As_2S_3 sols, the difference in appearance of the deposited flakes has been described, together with its dependence on the nature and concentration of the coagulator.[1]

Perhaps this is also connected with the irregularity mentioned on p. 424, that at the flocculation values the quantities of ions adsorbed are not always strictly equivalent.

The theory developed above (p. 442) would also be in agreement with this. At a small coagulator concentration the number of effective collisions is small, in a given time comparatively few primary particles will have had an opportunity to combine. With a high coagulator concentration almost all encounters are effective; the opportunity is favourable to the formation of large flakes. From this it also follows as a matter of course that the number of particles which remain behind as a residue without entering the large flakes is larger for small electrolyte concentrations, and smaller for larger ones, in agreement with the portion CD of the curve (Fig. 107).

The different rate of sedimentation of particles of various size and density also brings about the formation of layers, which can so often be observed in the sediment from a suspension and has attracted attention particularly in agricultural chemistry.[2]

The Velocity of Slow Coagulation in its Dependence upon the Concentration of the Disperse Phase

It is by no means a simple matter to determine the influence of the concentration of the disperse phase upon the C.V.[3] It is in general not permissible to compare various preparations of different concentration with one another. For even if the conditions of preparation have been kept sufficiently constant, the process is not so completely under control that all properties, such as the mean size of the particles, their distribution among the different sizes, the content of active electrolyte, etc., remain comparable in spite of the difference in concentration. It has hitherto been considered preferable to compare sols obtained by diluting a concentrated sol. Nor is this quite free from objection. Dilution with the dis-

[1] *Freundlich*, Zeitschr. f. physik. Chemie, **44**, 155–156 (1903).

[2] See e.g. *Ehrenberg*, Frl. *E. Hahn* and *Nolte*, Kolloidzeitschr. **21**, 1 (1917).

[3] See in this connexion particularly Kruyt and *van der Spek*, Kolloidzeitschr. **25**, 1 (1919); *Mukherjee* and *Sen*, Journ. Chem. Soc. **115**, 461 (1919).

persion medium may have a peptizing action (cf. p. 471); hence it is possible that coarser particles contained in the original sol may be split up. Further, dilution causes the concentration of active electrolyte to be diminished; this may bring about a stronger charge on the micellæ and hence increased stability. When therefore the argument, given below, is applied to sols prepared by dilution of more concentrated ones, we must bear these objections in mind.

A further difficulty is to secure really comparable coagulator concentrations. If equal amounts of the sol containing different amounts of disperse phase are mixed with equal amounts of a given electrolyte solution, by no means identical conditions result; in a concentrated sol, containing say twice as many particles, a larger amount of the active ion will be adsorbed; accordingly, its concentration after flocculation is smaller than in the more dilute sol. These different concentrations in the solution correspond to different amounts adsorbed. If, therefore, measuring everything in comparable units, γ is the original concentration after addition of electrolyte and before adsorption and flocculation, c_1 the concentration after flocculation in the more dilute sol, c_2 the corresponding concentration in that of double strength, a_1 and a_2 the respective amounts adsorbed, then

$$\gamma = c_1 + a_1 \text{ and } \gamma = c_2 + 2a_2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Now the form of the adsorption isothermal causes a_2 to be in general but slightly different from a_1. Hence c_2 must be decidedly smaller than c_1, and we ought to take instead of the value γ a larger one γ^1 in order to reach the same conditions of concentration. Hence the flocculation value must increase with increasing concentration of the sol. This is actually the case for the flocculation of As_2S_3 sols by bi- and tervalent kations (see Fig. 110). In this figure the concentrations of the sol are plotted as abscissæ, as ordinates the ratios β of the flocculation values; in calculating these ratios, the value found for the largest colloid content has been taken as unit.

For the univalent $K^{\cdot}$ ion this relation does not hold; indeed, there is a small decrease in the flocculation value with increasing concentration of the sol. But this too is intelligible. For univalent kations the flocculation values are much greater (see Table 112, p. 420). The amounts adsorbed remain, however, of the same order of magnitude as for multivalent kations. They are therefore small and may be neglected in comparison with the concentrations in the solution.[1] From equation (1) we have therefore

$$\gamma = c_1 = c_2$$

and hence the flocculation value should be independent of the concentration of the sol.

For $K^{\cdot}$ ions this is, however, as Fig. 110 shows, only approximately true. A fall in the flocculation value with rise of concentration is unmistakable. Now we must remember that the flocculation value denotes a concentration which produces a given transformation in a given time. If we assume that a relation holds for slow coagulation similar to that of the rapid (p. 434), then the time required for a given transformation should be greater, the smaller the initial content of the sol. In order to obtain

[1] Experiments by *Gann* (*loc. cit.* p. 416) with Al_2O_3 showed directly, in accordance with the positive charge of these sols, that with a univalent anion, such as Cl', the amount adsorbed amounts to a very small, analytically not measurable, fraction of the F.V.

in a given time in a dilute sol the same amount of transformation as in a concentrated one, a greater coagulator concentration must therefore be used; that is, the flocculation value would rise with falling concentration of the sol, as is actually observed with weakly flocculating ions, such as the $K^{\cdot}$ ion. In other words, the circumstance makes itself felt in dilute sols, that the greater mean distance between their particles renders coalescence to larger flakes less frequent. In this manner Kruyt and van der Spek,[1] and also Mukherjee and Sen,[2] explain the decrease in flocculation value with increase in concentration of the sol. With the more strongly flocculating ions this influence is also present, only the circumstance discussed above, resulting from adsorption, acts in the opposite direction and frequently preponderates. But not invariably. With sols which are already dilute, and whose particles adsorb only weakly, the increase in distance of the particles may so preponderate, even with strongly adsorbable and multivalent ions, that the stability of the sol increases with increased dilution. This was found by Mukherjee and Sen for HgS and CuS sols.

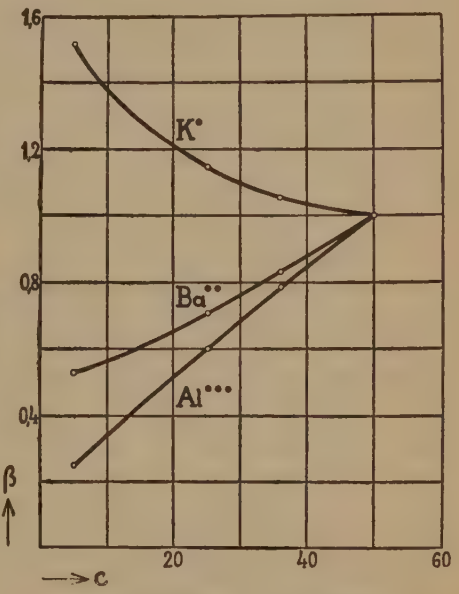

Fig. 110.—Dependence of Coagulation upon the Content of Disperse Phase.

Exactly the same difficulties as in the determination of the F.V. appear, when we attempt to determine the manner in which the whole course of slow coagulation depends on the concentration of the sol. We have the difficulty just referred to that comparable electrolyte concentrations are not readily obtained in the different sols. The comparison is again easiest in the case of the weakly adsorbable inorganic salts with univalent anions and kations, in which the concentration producing a measurably rapid coagulation is so great and the adsorbed amount in proportion so small, that the concentration in solution after adsorption may be regarded as unaltered. The series of experiments by Gann[3] can only be employed with great caution in judging the relation between C.V. and sol content, since the increase in viscosity does not give a clear picture of the increase in coagulation. His experiments seem to show that the constant $\varkappa$, calculated from the autocatalytic formula (see p. 436), increases somewhat with increasing sol concentration. This would agree with the requirements of Smoluchowski's theory, according to which in a more concentrated sol the same transformation requires a shorter time. This increase in $\varkappa$ with the sol concentration appears to be of the same order of magnitude as that which one would expect from the experiments of Kruyt and van der Spek for the decrease in F.V. with increasing sol content.

[1] *loc. cit.* p. 447. [2] *loc. cit.* p. 447. [3] *loc. cit.* p. 416.

In the foregoing considerations we must, as already pointed out, strictly speaking take into account the possibility that the dilution of the sols in itself alters their stability. It is conceivable that this stability may be increased, since the diminution in the concentration of active electrolyte increases the charge on the micellæ. This would likewise cause a higher F.V. for small sol concentrations.

It seemed to follow from the experiments of Gann that the C.V. curves for equal concentrations of the coagulator (KCl), but for different concentrations of the sol, are not affine; they are indeed, to some extent, for small concentrations (up to about 1·3 grm. Al_2O_3 per litre in the experiments in question), but not for greater ones, in which the point of inflexion of the autocatalytic curve appeared to be obscured and to approach the initial point of the curve. v. Smoluchowski,[1] however, pointed out that this only arises from the want of proportionality—as discussed above on p. 417—between the increase of viscosity in the more concentrated sols and their content of coagulated particles. If this is suitably taken into account, the curves, calculated relatively, for the increase in viscosity of sols of different content with time, are found to coincide. The curve thus obtained retains its S-shape, which is, however, referred by v. Smoluchowski to the change in the active volume of the particles and consequent influence on the viscosity of the sol (cf. p. 440).

The dependence of the C.V. on the number of particles may be determined more definitely through the sedimentation of coarse suspensions than through the coagulation of sols. For here the danger is less that dilution occasions a further diminution in size of the primary particles. If we further use with a negative suspension a univalent kation as coagulator, the conditions of adsorption are also fairly constant. Odén [2] found that with kaolin suspensions of different content the flakes formed at equal concentrations of the coagulator differ very little in size. The aggregation time (cf. p. 442) is here therefore a true specific coagulation time, to which equation (7) on p. 434 may be applied. The product of aggregation time τ and number of particles ν_0 should therefore be constant. This is actually the case, as the following Table 122 shows. The concentration of the coagulator K_2SO_4 amounted to 100 millimol.

TABLE 122

Dependence of the Aggregation Time on the Number of Particles in the Sedimentation of Kaolin Suspensions

Kaolin Content, g. per l.	Number of Particles, ν_0 per c.c.	Aggregation Time τ in minutes.	$\tau \times \nu_0 \times 10^{-12}$.
0·26	4·4 $\times 10^9$	119	31·4
0·39	6·625 $\times 10^9$	84	33·5
0·78	13·25 $\times 10^9$	37	29·5
1·02	17·65 $\times 10^9$	29	30·8
1·53	26·5 $\times 10^9$	20	32·0
2·04	35·3 $\times 10^9$	15	31·7
3·06	53 $\times 10^9$	11	35·0

[1] Zeitschr. f. physik. Chemie, **92**, 158 (1917).

[2] *loc. cit.* p. 441.

Detailed experiments on the influence of the size of the particles on the C.V. are not yet available for the more hydrophobic sols. It is probably similar to that which we shall encounter later (p. 622) with Odén's sulphur sol.

The foregoing considerations relate to sols with practically spherical particles. How far do they remain valid, if the particles have a distinctly different shape? The F.V. of vanadium pentoxide sols, the particles of which are rod-shaped (cf. p. 404), obeys quite the same laws as were found to hold for spherical particles.[1] The F.V. indeed varies greatly for different univalent kations; the lyotropic series is much more pronounced than is usually the case; $Li^{\cdot}$ has the largest and $Rb^{\cdot}$ the smallest F.V. This is not, however, connected with the shape of the particles, but almost certainly with the strong hydration of the micellæ, and hence with the fact that this sol approaches the hydrophilic ones (see p. 427). The same strong dependence upon the lyotropic order of the kations is found for Mo_2O_5 sol, the particles of which are not rod-shaped, but which also is allied to the hydrophilic sols.[2]

But the shape of the particles will certainly affect the numerical coefficients, which have to be taken into account in v. Smoluchowski's theory (see p. 432); for the diffusion of the particles, and hence also the conditions for the coalescence of single and multiple particles, are influenced by their shape.

An influence of the shape of the particles will also make itself felt in the phenomenon considered on p. 437, that stirring so greatly favours flocculation, if the particles are large enough. This influence of stirring will probably be much smaller with rod-shaped particles than with spherical, for since the particles set themselves during stirring with their axes in the direction of the current, they only offer their narrowest surfaces for collision. Upon this probably depends the fact that the particles of V_2O_5 sols, even when they are very large, have so slight a tendency to settle.

Another Conception of Coagulation

The foregoing description of the processes of coagulation has purposely been somewhat simplified in order to bring out more clearly, by means of a sharper picture, the points of attack for further experiment. In various cases facts have been mentioned which cannot straight off be reconciled with the views which have been developed. For instance, the coagulation of As_2S_3 sols by KCl proceeds at a ζ value which is much higher than that necessary with kations of higher valency (see p. 419). Further, the strongly marked lyotropic series of the alkali metal kations in the coagulation of strongly hydrated negative hydroxide sols is remarkable (cf. p. 427). It could be ascribed with great probability to the hydration of the micellæ; the less hydrated micellæ of Weimarn's sulphur sol did not show this behaviour, the strongly hydrated micellæ of Odén's sulphur sol showed it strongly. Further striking examples of a hitherto unconsidered influence of hydration will be met with later (p. 461) in coagulation by mixtures of electrolytes. As has already been pointed out, we are probably dealing here with a hitherto unconsidered effect of the hydration of micellæ and

[1] *Freundlich* and *Leonhardt*, Kolloidchem. Beihefte, **7**, 187 (1915).

[2] *Freundlich* and *Leonhardt*, Kolloidchem. Beihefte, **7**, 172 (1915): see also the note that the sol is one of Mo_2O_5 and not of MoO_2 [Kolloidzeitschr. **17**, 112 (1915)].

coagulators on the stability of the sols. These are therefore the same circumstances which determine the solubility of truly dissolved substances. Hence the theory given above would only be strictly applicable to thoroughly hydrophobic sols, therefore to oil emulsions, sols of the metals, S_λ sulphur sols; much less to the more hydrophilic hydroxide sols. The sulphide sols are intermediate.

Pauli and Matula [1] and, at an earlier date, although in a somewhat different fashion, J. Duclaux [2] were inclined to regard the stability of sols mainly from the point of view of solubility, coagulation therefore as the separation of a difficulty soluble electrolyte, in which the micellæ are simply to be regarded as large colloid ions. This conception has in any case to be amended on account of certain peculiarities of colloid ions. They accordingly regard in Fe_2O_3 sols that part of chlorine which cannot be recognized potentiometrically as Cl′ ion, as non-dissociated, and therefore reject Maffia's above-mentioned conception (p. 372) of an adsorption of the Cl′ ion. They believe themselves able to advance arguments in proof of the dissociation theory, such, for example, as that the addition of an electrolyte solution, which is equally concentrated in Cl′ ions, produces in an Fe_2O_3 sol no displacement in the Cl′ ion concentration of the sol; further, that under certain circumstances the kations of an added electrolyte may also decrease in concentration, which fact they refer to a depression of the dissociation by the dissociated ferric salt of the sol. Neither argument is valid, however. For, if the Cl′ ion in the Fe_2O_3 sol is in adsorption equilibrium, the equilibrium must of course be maintained, if the Cl′ concentration remains unaltered. And that the anions contained in the intermicellar liquid are so free, that they are able to depress the dissociation of an added salt with the same anion, entirely agrees with the general view of the equilibria existing in the sol. Moreover Pauli and Matula also emphasize that the behaviour of sols as regards conductivity cannot be interpreted simply from the point of view of the dissociation theory.

With Zsigmondy [3] I should like to question whether we have cause to differentiate completely this dissociation equilibrium of a salt with highly complex kations, such as Pauli and Matula attribute to a Fe_2O_3 sol, from the adsorption equilibrium of a salt on a micella. We are dealing with a comparatively large molecular complex, to which other atoms, molecules, or ions are bound by a part of the valency forces, while the rest of these forces serves to maintain unaltered the structure of the complex (cf. p. 235). Only in so far as hydration is important in the formation of solution molecules, and therefore in true solubility, only in so far as it is also of influence upon the equilibrium of the micellæ, do we have to take this circumstance into account more extensively than was done in the theory of coagulation developed above (p. 418).

Further, we must also remember the following. The theory of dissociation, particularly that of organic electrolytes, is at present by no means a perfectly solid and secure foundation on which to build (cf. p. 49). I would rather suggest that in course of time a more trustworthy basis will be found for this theory, in kinetic considerations, such as have now already been applied with success to the theory of coagulation—for example, the Zsigmondy-Smoluchowski conception of rapid coagulation.

[1] Kolloidzeitschr. **21**, 49 (1917); *Pauli, ibid.* **26**, 20 (1920).
[2] Journ. d. chim. phys. **5**, 29 (1907); **7**, 405 (1909).
[3] Kolloidzeitschr. **26**, 67 (1920).

FIG. 111A.

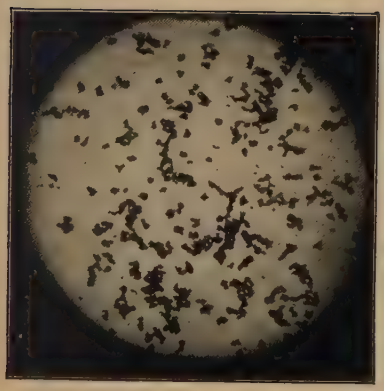

FIG. 111B.

FIG. 111C.

To face page 452.]

The Coarsening of Coagulated Flocculi. The Reversal of Adsorption

The circumstance just discussed (p. 446), that the flocculi have a different composition according to the nature and concentration of the coagulator, also appears clearly in the following fact. The flocculi are not deposited in a state of equilibrium, but suffer in course of time further changes, dependent upon the concentration of the coagulator. Their very appearance shows this, particularly that of sulphide and hydroxide sols. While the flocculi are at first spongy or gelatinous and constitute a layer several centimetres thick in a glass cylinder, they become after a few hours or days gritty and sandy, and only form a layer a few millimetres thick upon the bottom of the vessel. The photomicrograph obtained with a HgS sol (see Fig. 111 A, B, and C on Plate III) show this change of the flocculi quite plainly.

The direct investigation of the kinetics of this *coarsening process* would be extremely difficult; we would not know what property of the flocculi should be chosen as characteristic of the change with time. Under certain as yet obscure circumstances another process, more easily followed, takes place along with the coarsening. If, for example, a HgS sol (with which the phenomenon has been chiefly investigated [1]) has been coagulated by a dye such as new fuchsine, it may very well occur that at first the dye kation has been practically completely adsorbed by the flocculi, so that the supernatant liquid appears colourless. Now while the flocculi coarsen, the liquid becomes redder and redder, probably because the flocculi reduce their surface and hence give up adsorbed dye. This phenomenon is therefore known as *adsorption reversal.*

That this recoloration of the liquid is causally connected with the alteration in the coagulated particles results particularly clearly from experiments with a sulphur sol,[2] which must be discussed here, although this sol will be considered systematically later under the lyophilic sols. It, too, may be coagulated with new fuchsine in such a way that the supernatant liquid is almost colourless. On shaking or centrifuging the coagulated sulphur flakes collect at the bottom of the vessel in the form of a few viscid globules or of a cake, which is coloured red by adsorbed dye. If these globules are allowed to remain quietly on the bottom of the vessel, we can soon recognize a strongly coloured zone of liquid surrounding them. If the adsorption reversal has proceeded for some time, the sulphur globules become less viscid, their parts no longer stick together so well, and finally they fall apart into a mass of flakes which are however quite different from the original flakes obtained immediately after coagulation. They have unmistakably much rougher edges, are more sharply defined, and apparently crystalline. While the original flakes unite on centrifuging to a cake on the bottom of the vessel on account of their stickiness, these flakes formed by the disintegration of a cake are extremely fine, they do not stick together, and even after centrifuging it is extremely difficult to pour off a clear solution, since some of the flakes float on top of the liquid.

[1] *Freundlich* and *Schucht*, Zeitschr. f. physik. Chemie, **85**, 660 (1913); *Freundlich* and *Hase, ibid.* **89**, 417 (1915). As further examples may be mentioned the behaviour of a gel separated from a CeO_2 sol [*Fernau* and *Pauli*, Biochem. Zeitschr. **70**, 428 (1915)] and that of silver coagulated from an Ag sol [*Zsigmondy*, Nachr. d. Ges. d. Wiss. Göttingen, 1917, p. 35.]

[2] *Freundlich* and *Hase*, Zeitschr. f. physik. Chemie, **89**, 430 *et seq.* (1915).

During this transformation the colour of the liquid becomes continually deeper.

The course of this adsorption reversal and hence of the coarsening of the flakes can be followed by determining colorimetrically from time to time under uniform conditions of stirring the dye-content of samples of the liquid freed from flakes. As far as the difficult experiments have gone, they seem to bring out a striking similarity between the velocity of the adsorption reversal and that of slow coagulation. As before, it of course remains an open question how far the course here observed is really to be ascribed to the actual coagulation. In Fig. 112 the abscissæ are the times in minutes, the ordinates the dye concentrations in the liquid; the sol is HgS, flocculated by auramine.

Here also there is a pronounced autocatalytic course. The velocity rises extremely rapidly with the coagulator concentration. This may be varied here also, since a lower coagulation zone exists (cf. p. 429) within which various coagulator concentrations may be employed. The coagulator concentration cannot be increased at will, since all these dyes show an irregular series in flocculation; at larger coagulator concentrations the micellæ have their charge reversed and the sol again becomes stable. The enormous rise in velocity with the coagulator concentration is seen in Fig. 112. As in the case of the coagulation velocity (p. 442), it may be quite well represented by an equation

$$\varkappa = \text{Const.} \times a^p$$

where $\varkappa$ is the velocity constant of the adsorption reversal, a the amount adsorbed by the flakes, and p the exponent with a value between 2 and 7.

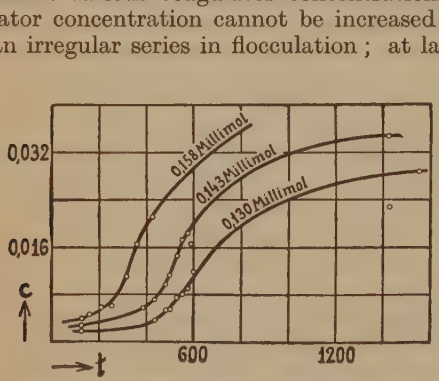

Fig. 112.—Velocity of Adsorption Reversal with various Coagulator Concentrations.

According to the results with the C.V. no theoretical value can be attached to this formula, the less so in this case, since for large amounts adsorbed the adsorption reversal becomes meaningless, because coagulation does not take place on account of the irregular series. But the similarity of the two phenomena is certainly characterized by the similarity of the formulæ which apply to them.

The velocity curves found for various coagulator concentrations are again affine, as in the case of the C.V. Therefore, even if the total course is not expressed by a formula, we can nevertheless represent the dependence of the velocity upon the coagulator concentration by numerical values (see p. 442).

This behaviour of coagulated flakes in becoming coarser may be explained in a similar manner to that of slow coagulation. The flakes, as they settle after coagulation under the influence of gravity, are not without charges, for flocculation already occurs below the first critical potential, but still above the second. Nor, as Zsigmondy [1] rightly points out, is it necessary that the single particles in the freshly coagulated flakes should be directly united; they may very well be still separated by ultramicroscopic liquid

[1] Nachr. d. k. Götting. Ges. and Wiss., 1917, p. 33.

films. The portion of the charge which still remains, and these liquid films, are what determine the further coarsening of the flakes. In their loose union the single particles will still carry out oscillatory molecular movements. This may be seen under the ultramicroscope when several particles have united to a group during flocculation. Even now the residual charge will determine a repulsion, which is the greater, the greater this charge, and only those particles which collide with a certain critical force will come into direct contact, unite more completely, and coalesce. The velocity of coarsening and hence the reversal of adsorption will be proportional to the number of these sufficiently rapid particles. The necessary critical force is smaller when the charge is smaller and the coagulator concentration greater—assuming that no reversal of charge has yet taken place beyond the iso-electric point. The greater the coagulator concentration, and hence the smaller the charge, the greater also the number of particles which have the necessary force, the greater therefore the velocity of coarsening and of adsorption reversal.

This theory, perhaps wrongly, neglects the fact that the flakes contain varying numbers of primary particles at various coagulator concentrations.

Further Phenomena connected with the Coarsening of Flakes

The previous section does not exhaust the number of these phenomena. The time processes which lead to the formation of colloid particles of ordinary size appear to be of a similar character. When two dissolved substances react with formation of a difficulty soluble precipitate, particles of ordinary colloidal size are of course not the first product to be formed; at the first moment single molecules of the new substance are certainly present, and very soon also minute particles consisting of a very few molecules. It has indeed been impossible to measure directly the coarsening of these finest aggregates to ordinary colloid particles, but the occurrence and progress of this coarsening seems once more to reveal an adsorption reversal. Anyhow, C. L. Wagner [1] explains in this way the so-called slow hydrolysis of ferric chloride first observed by Goodwin.[2] Ferric chloride and related salts appear to hydrolyse slowly in very dilute aqueous solution, as shown by the gradual increase in conductivity. Now such a slow hydrolysis is improbable on other grounds. C. L. Wagner therefore believes that the hydrolysis itself is quickly at an end, but that the hydrochloric acid formed at first remains adsorbed on the newly formed Fe_2O_3 particles, and is gradually given up as the particles become coarser. This view is supported by the fact that the course is autocatalytic, as in the reversal of adsorption, and that anions—such as SO_4''—which flocculate strongly at low concentrations, hasten this "hydrolysis."

The slow hydrolysis of potassium ruthenochloride [3] also follows quite similar rules, and is probably to be explained in a similar way as an adsorption reversal.[4]

Apparently therefore all processes in which colloid particles become coarser proceed according to the same or at least very similar laws:

1. The formation of ordinary colloid particles from the extremely fine particles which arise at once, as a result of the chemical reaction generating the new substance (slow hydrolysis).

[1] Wien. Monatshefte, **34**, 95 (1913).
[2] Zeitschr. f. physik. Chemie, **21**, 1 (1896); Phys. Rev. **11**, 193 (1900).
[3] *Lind* and *Bliss*, Journ. Amer. Chem. Soc. **31**, 868 (1909).
[4] *Freundlich* and *Hase*, Zeitschr. f. physik. Chemie, **89**, 457 (1915).

2. The ordinary slow coagulation of the colloid particles up to the formation of the freshly coagulated flocculi.
3. The coarsening of the coagulated flocculi.

These facts suggest the idea that in a sol flocculation does not necessarily proceed smoothly when it has once begun, but that widely different stationary states may persist for a considerable time. These states cannot rightly be described as equilibria, since, as already remarked (p. 415) under ordinary experimental conditions, the equilibrium distribution of the micellæ of sols has certainly been but rarely investigated.

A few examples of this kind may be given. Linder and Picton [1] describe the case of an As_2S_3 sol, which originally contained such small particles that they passed through a porous pot. After addition of a few drops of dilute NaCl solution the stability was externally unaltered, but the particles no longer passed through the filter; they had apparently increased in size.

Further, the *ageing* of sols comes under this heading. Many sols show immediately after their preparation various comparatively rapid changes in their properties, while after some time a less changeable stationary state is reached. Thus, according to R. O. Herzog,[2] the viscosity of an As_2S_3 sol declines markedly in the first weeks. Since it is probable from the experiments of Woudstra (cf. p. 439) that this decrease in viscosity is associated with a coarsening of the particles, we might perhaps have here also, as in the above-named case of ferric chloride, a coarsening of the particles at first formed. With other sols such ageing shows itself by a change of the charge on the particles or in a consequent alteration in the F.V. Thus Powis [3] describes a decrease with time of the charge measured kataphoretically on the drops of an oil emulsion, which remarkably enough is particularly evident, when a slow flocculation by small electrolyte concentrations has set in; that is to say, immediately after addition of the electrolyte a rapid change of charge at an indeterminable rate first sets in, to be followed by a further change which proceeds comparatively slowly. With an As_2S_3 sol, to which KCl had been added, Powis [4] could not observe a similar change of charge. Freundlich and Schucht [5] mention an appreciable decrease with time in the F.V. of As_2S_3 sols on flocculation with $Al_2(SO_4)_3$, and Gann [6] remarks that the C.V. of an Al_2O_3 sol under the influence of electrolytes such as NH_4Cl clearly increases by a few per cent. in the first days after preparation, while after some weeks it remains practically constant during many months. According to Bredig and Ikeda [7] the catalytic activity of a Pt sol alters in the first days after its preparation, but then remains unchanged for weeks.

At present these processes cannot be explained at all readily. Perhaps no general explanation can be correct, and a different one is required from case to case according to the chemical nature of the micella. We might imagine that, by means of coagulator concentrations so small that the discharge does not proceed to the first critical potential, the flakes are nevertheless coarsened; only they do not become large enough to settle. This would only be a further consequence of the phenomenon described

[1] Journ. Chem. Soc. **67**, 73 (1895).
[2] Kolloidzeitschr. **8**, 210 (1911).
[3] Zeitschr. f. physik. Chemie, **89**, 179 (1915).
[4] Journ. Chem. Soc. **109**, 734 (1916).
[5] Zeitschr. f. physik. Chemie, **80**, 566 (1912).
[6] Kolloidchem. Beihefte, **8**, 84–85 (1916).
[7] Zeitschr. f. physik. Chemie, **37**, 2 (1901).

above for coarse suspensions (cf. p. 446), that the number of primary particles contained in the flakes decreases rapidly with the coagulator concentration. The first critical potential would then be characterized by the formation of coarse flakes which settle. The initial ageing would further be explained by the absence of equilibrium between the freshly formed micellæ and the electrolytes of the liquid, and further by the fact that the setting-up of this equilibrium consists in a union of primary particles to larger, although still very small, ones. The experiment of Linder and Picton (see p. 456) would thus also be susceptible of ready explanation. The slight addition of NaCl causes the production of somewhat larger aggregates, which, owing to their lively Brownian movement, are still small enough to give a stable sol, but already too large to pass through a porous pot. Of course the other possibility cannot be excluded *a priori*, that substances which in course of time are formed in the sol (in the case of As_2S_3 sols, for instance, H_2S and As_2O_3) peptize the flakes and counteract a flocculation which has already set in.

An investigation of the charge of freshly formed sols which are gradually approaching a stationary state is moreover still entirely wanting. We do not know whether the micellæ of such a sol in a stationary state have a potential which corresponds to the maximum potential, that is, to the point B of Curve 2, Fig. 50, p. 259, or whether the charge on the particles and their stability may be raised by the addition of minute amounts of electrolytes.

All the circumstances just discussed—the autocatalytic shape of the C.V. curve, the influence of coarser flakes upon coagulation, the coarsening of flakes and the ageing of sols—all these no doubt contribute to the remarkable phenomenon, observed with most if not all sols, that the manner of mixing coagulator solution and sol has an important effect on the course of coagulation. Thus, with an As_2S_3 [1] sol the following was found. If a given amount of $BaCl_2$ solution, which, if all added at once, completely flocculated in 2 hours, was added drop by drop in the course of 18 hours, 25 or 45 days, the sol was in the latter cases by no means completely flocculated two hours after the completion of the addition, but was still very turbid, and about an equally large amount of coagulator solution, of the same concentration as was necessary for the unaltered sol, was required to produce complete flocculation. Similar results were obtained with a platinum sol; this effect was less marked although still distinct, with a Fe_2O_3 sol. If we are therefore on a C.V. curve for small coagulator concentrations at some distance from the initial point, we do not by addition of further electrolyte simply arrive reversibly at one of the C.V. curves such as are obtained when the greater coagulator concentration has been added to the sol at the outset. This behaviour also is most easily understood by taking up the standpoint described above (p. 446)—the smaller the coagulator concentrations the smaller the flakes resulting. If such an amount of coagulator is immediately added that the concentration in the sol is high, large flakes will be formed according to the steepest curve, for 95 millimol, in Fig. 107; only a very small fraction of the primary particles—corresponding to the part CD of the curve—does not go into the flakes. But if only a small amount of coagulator is added, small flakes are formed according to the curve for 5·95 millimol. A further amount added after

[1] *Freundlich*, Zeitschr. f. physik. Chemie, **44**, 143 *et seq.* (1903).

some time meets with other conditions than that at first added; the adsorbing surface, for example, will be different, for with primary particles in the flakes, the part of the surface lying towards the inside will take little or no part in the adsorption. Larger flakes will now indeed be formed corresponding to the larger coagulator concentration; these will, however, in so far have a different character as they have in part been formed by the union of smaller flakes already present, and not from a large number of equally discharged primary particles, as is the case when a larger coagulator concentration is used from the first. With gradual addition of electrolyte the flakes are actually less dense, more spongy and looser, than with rapid addition of electrolyte. Particularly under these conditions a large number of primary particles and smaller flakes will remain excluded from the larger ones, corresponding to a very long range for CD, as, for instance, in the curve with 5·95 millimol NH_4NO_3 in Fig. 107.

Evidently, also, the other circumstances affecting the ageing of sols may play a part during the long period required for the gradual addition of the coagulator.

But the processes discussed above must further be considered in a much more general manner, especially in all cases where a solid precipitate is formed in a liquid, whether by evaporation of the supersaturated solution of a solid, or by chemical interaction. The production of a solid phase of sufficiently great dispersity in a liquid is, however, simply the production of a colloidal solution. The theory of the preparation of sols presupposes a knowledge of these phenomena.

The conditions are relatively simplest, although still complex enough, when the colloid particles are small crystals, as in the case of gold and silver sols. In the separation of the metal from the reacting solutions nuclei must first of all be formed, with their characteristic rate of formation of nuclei, according to the considerations on p. 322. These nuclei grow, with the characteristic velocity of crystallization likewise proper to them, into the crystals contained in the sol. In the case of gold sols Zsigmondy has already largely elucidated how the great and still obscure dependence of the velocities of formation of nuclei and crystallization upon minute concentrations of foreign substances permits, in the most favourable case, of the preparation of a sol with particles of a definite order of magnitude. In the special part this will be considered in detail (p. 502).

If the particles formed are at first amorphous-solid, they may pass through a series of intermediate stages; for the present we leave it undecided whether the amorphous-solid particles are so small that they remain in colloidal solution, or whether they separate as larger flakes, which, becoming coarser, finally crystallize, as discussed above (p. 453) in connexion with the reversal of adsorption. From the nuclei first formed small amorphous-solid flocculi therefore arise—as in the case of the hydrolysis of ferric chloride (p. 455)—these coagulate to larger flakes, perhaps influenced by electrolytes contained in the solution; from the larger flakes crystals may further be formed (cf. p. 453), and at all these stages we have to deal with the velocity processes already discussed. There is a further question as to the connexion between the coarsening of coagulated flakes and the crystallization velocity in the ordinary sense. It may be that nuclei of the crystalline phase must first be formed inside the flakes, which then grow further at the rate of crystallization proper to them. We might thus possibly have in the formation of a crystalline solid precipitate in a solution to consider the following chain of processes:—

Homogeneous solution $\longrightarrow$ nuclei of new phase $\longrightarrow$ amorphous sub-
(Velocity of formation of nuclei of new phase) (Velocity of formation of colloidal
microns $\longrightarrow$ coagulated flocculi $\longrightarrow$ coarse flakes $\longrightarrow$ crystal nuclei
solution) (Coagulation velocity) (Velocity of coarsening) (Rate of formation of nuclei of the crystalline phase)
$\longrightarrow$ coarse crystals
(Velocity of crystallization)

As already said, it must remain an open question whether we have the right to distinguish between the growth of flakes and actual crystallization, or whether the same constants apply to both cases.

Anyhow, the production of a solid substance in a solution is an extremely complicated process. It is therefore intelligible that the appearance of solid precipitates may differ so greatly, and that apparently unimportant changes in the composition of the solution produce great changes in the structure of the precipitate. Where the object is the production of such precipitates with definite properties, as in the case of colloidal solutions or of silver mirrors, carefully tested directions are therefore necessary. In the case of colloidal solutions, which contain amorphous-solid particles, it has not yet been possible to determine the decisive influences in detail; more nearly perhaps in the case of silver mirrors, which will be discussed later (p. 742).

In contradiction to the opinion here maintained, v. Weimarn [1] has developed a theory according to which the separation of a solid phase is very generally and uniformly regulated by its solubility and by the supersaturation prevailing. What is known concerning the extraordinary sensitiveness to foreign substances of the velocities of formation of nuclei and crystallization makes it *a priori* improbable, and experience has not confirmed this theory.[2] Only two statements of Weimarn's appear to have a more general validity. The first is, that when reacting solutions are very dilute, the resulting solid appears in a plainly crystalline form. At the low concentration the velocity of formation of nuclei is very small, and the few nuclei formed grow slowly at the cost of the solid present in weakly supersaturated solution—conditions favourable to the formation of crystals Secondly, that conversely, when the reacting solutions are very concentrated, jellies are often easily formed. These consist of drops of the liquid surrounded by films of the solid reaction product. At the high concentration the rate of formation of nuclei is extremely high; when and where the two liquids touch, the resulting nuclei directly form a felt-work without having had time for further crystallization and constitute what is probably an amorphous-solid film. A further crystallization only occurs when the dissolved substances have penetrated to each other through the film.

Flocculation by Mixtures of Electrolytes

Matters immediately become more complicated when more than one coagulator acts. One ought really to determine C.V. curves and determine the adsorption isothermal for all the ions concerned. Such investigations are not yet available. So far, experiment has gone no further than determining flocculation values in the presence of several electrolytes under various conditions. Coagulation by mixtures deserves, however, to be considered in detail, since it is important in various respects. In the first

[1] E.g., Kolloidzeitschr. **2**, 199, 230, 275, 301, 326 (1908); Supplement b. II, p. LII (1908); **3**, 39, 282 (1908); **4**, 27 (1909).

[2] *Büchner* and *Kalff*, K. Akad. v. Wetensch., Amsterdam, **28**, 145 (1919); *Bancroft*, Journ. Phys. Chem. **24**, 100 (1920).

place it is more often met with in practice than coagulation by pure electrolytes; particularly in biological processes we are always dealing with coagulation by several electrolytes. Further, influences come into play which are much less important in the flocculation by pure electrolytes, and differences between sols appear which otherwise are scarcely noticeable.

What behaviour is to be expected from the adsorption theory above developed? We will consider a negative sol, neglect the influence of the anions, and only take the discharging effect of the kations into account. We may further reckon for the present with the following assumptions. According to the rules for the adsorption of several substances (p. 206) the adsorption of both kations will be lowered, that of the more weakly adsorbable relatively more than that of the more strongly adsorbable; further, we may assume that the amount a_k of kation adsorbed which is required for the same amount of discharge to be effected and for a definite comparable F.V. to be attained, is, reckoned in equivalents, as great in the mixture as for coagulation by a single kation. We should then expect that the flocculation values of the kations in mixtures would, in general, be smaller than those of the single kations in pure solution; for the amounts adsorbed a_k' and a_k'' of the two ions must be smaller since their sum is to be equal to a_k. An increase in the F.V. of a kation in the mixture might indeed occur if its adsorption isothermal were very strongly depressed by the presence of the other kation. The possibility then exists that the concentration which is in equilibrium with the smaller amount adsorbed a_k' is greater than that which in the pure solution is in equilibrium with a_k. An increase of this kind will most readily be possible with weakly adsorbable ions, such as the alkali kations. But it is improbable that it would amount to more than 20–50 per cent.

A behaviour of this kind is, according to experiments by P. Scholz,[1] present to a large degree with decidedly hydrophobic sols, such as a gold sol (Donau's) and a sulphur sol (v. Weimarn's; see p. 427). The measurements were carried out by first adding to the sol a solution of LiCl in a concentration which was a fraction of that required for coagulation in pure solution, a fraction which moreover produced no recognizable change in the sol in a short time. This sol containing LiCl was then used for the determination of the F.V. of other electrolytes in the usual manner. LiCl was chosen in particular because it had shown very striking departures from the expected behaviour in the case of more hydrophilic sols. Table 123 for a gold sol

TABLE 123[2]

Influence of the Presence of LiCl upon the Coagulation of a Gold Sol

Content of LiCl in percentages of the F.V. in pure Solution.	F.V. (in percent. of F.V. in pure solution) of				
	KCl.	$MgCl_2$.	$BaCl_2$.	$AlCl_3$.	$CeCl_3$.
0	100 (18)	100 (0·15)	100 (0·13)	100 (0·0022)	100 (0·0022)
20 (4·5)	66 (12)	73 (0·11)	60 (0·078)	62 (0·0014)	36 (0·00079)
40 (9)	55 (9·8)	66 (0·10)	46 (0·06)	30?(0·0007)	30 (0·0007)
60 (13·5)	50 (9)	60 (0·09)	38 (0·049)	38 (0·0008)	23 (0·0005)
80 (18)	33 (6)	50 (0·075)	30 (0·04)	25 (0·00055)	20 (0·0004)

[1] Unpublished.

[2] The figures in brackets denote the content or F.V. in millimol per litre.

shows that the F.V. is throughout smaller for the mixture than for the pure solution. The figures are percentages of the F.V. in pure solution. They are all below 100 per cent.

Similar results were obtained with a Weimarn sulphur sol, and the same may be concluded from the experiments of Bender [1] on a mastic sol, for the coagulation of which HCl was mostly taken as one of the electrolytes.

TABLE 124

Influence of the Presence of LiCl upon the Coagulation of an As_2S_3 Sol

LiCl Content in percent. of F.V. in pure Solution.	F.V. (in per cent. of F.V. in pure Solution) of			
	$MgCl_2$.	$BaCl_2$.	$AlCl_3$.	$CeCl_3$.
0	100 (0·6)	100 (0·5)	100 (0·03)	100 (0·03)
25 (24)	200 (1·2)	133 (0·66)	110 (0·033)	65 (0·019)
50 (48)	220 (1·3)	>110 (>0·55)	133 (0·04)	about 100 (about 0·03)
73 (70)	233 (1·4)	>110 (>0·55)	166 (0·05)	about 100 (about 0·03)

But already with an As_2S_3 sol (Table 124), which we are accustomed to regard as very hydrophobic, striking departures from this behaviour occur, similar to those we shall encounter later, but which are much more strongly marked, in the case of more hydrophilic sols (p. 620). The most remarkable point is the mutual action of LiCl and $MgCl_2$. It is in the sense that the $Li^{\cdot}$ ion makes the sol more stable towards $Mg^{\cdot\cdot}$ ions; a higher concentration is necessary for coagulation than in pure solution. The F.V. of the $Mg^{\cdot\cdot}$ ion, which ordinarily lies at about 0·6 millimol per litre, is raised to more than double by the $Li^{\cdot}$ ion. We have an *antagonistic mutual action* of the kations. With $Al^{\cdot\cdot\cdot}$ ions an influence of this kind is still noticeable, less readily with $Ba^{\cdot\cdot}$ ions. An antagonistic action of this kind was first very clearly found by Neuschloss [2] for lecithin sols (cf. p. 647), which, as decidedly more hydrophilic, will not be discussed until later.

This rise in the F.V. cannot depend upon the fact that, as mentioned above, the F.V. of a kation in a mixture may sometimes be increased by the depression of its adsorption isothermal. In the first place the increase is much too great for that. A still more important objection is the fact that differences in kations appear in this connexion which are wholly or almost wholly obscured in the flocculation values in pure solution. So far the most clearly marked antagonism was that between Li and Mg—perhaps still more strongly that between Li and Be. It decreased very much in passing from Mg to Ca, Sr and Ba, although the F.V. of these bivalent kations for gold as well as for As_2S_3 sols differs only slightly. It also decreased (as deduced in part from experiments on more hydrophilic sols) when Na was substituted for Li; it practically disappeared for K. Along with it an influence of the anions was noticeable. In any case those ions are prominent which are regarded as strongly hydrated. We have therefore every reason to suppose that here the influence of hydration makes itself felt, which was already suspected above (p. 426) in the lyotropic series of the

[1] Kolloidzeitschr. **14**, 255 (1914).
[2] Pflüger's Archiv, **181**, p. 17 (1920).

kations and the aberrant behaviour of As_2S_3 sols in respect of the first critical potential with univalent kations.

The phenomenon becomes much less distinct when ions less hydrated than Li, Mg, etc., are employed. Linder and Picton [1] however point out that with As_2S_3 sols univalent kations alone mainly behave additively, not so univalent mixed with bivalent; more of a bivalent ion is required for coagulation than corresponds to the additive behaviour. This is probably the same as the phenomenon just described. Freundlich and Pape,[2] on the other hand, on investigating the coagulation of As_2S_3 sols by $K^{\cdot}$ ions mixed with various other kations ($Na^{\cdot}$, $Ba^{\cdot\cdot}$, $Ce^{\cdot\cdot\cdot}$, strychnine), did not observe a behaviour of this kind. They used for special reasons a quite different method of measurement from that of Scholz; they measured the F.V. of solutions which from the start contained the kations mixed in a definite proportion and found for $K^{\cdot} + Na^{\cdot}$ an additive behaviour; for the other ions one that could be deduced from the adsorption isothermals in the manner described above for the gold sol. This is not in contradiction to the result of Table 124; for with slightly hydrated kations (for instance, if $H^{\cdot}$ ions were added and then the F.V. determined for $Ba^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$ and $Ce^{\cdot\cdot\cdot}$ ions) Scholz also obtained for As_2S_3 sols flocculation values which all lay well below 100 per cent., and thus corresponded to the behaviour with hydrophobic gold sols.

With still more strongly hydrophilic sols, such as Odén's sulphur sol and lecithin sols, this influence of hydration is met with in a still more pronounced form. Not only is the rise of the F.V. for the mixture greater, but differences between kations become noticeable which did not appear with the sols hitherto considered. This will be discussed later (p. 620).

The investigation of the behaviour of sols upon coagulation by mixtures of electrolytes is evidently a means of determining to what degree hydration relationships are important for stability. Experiments hitherto made do not provide a clear interpretation of these phenomena from a theoretical point of view.

A further question would be whether this influence of the hydration of the electrolytes also appears in electrokinetic phenomena with hydrophilic walls. The lyotropic series found by J. Loeb (see p. 270), for hydrophilic membranes made of collodion containing gelatine, tells in favour of this being the case.

The Sensitization of the Flocculation of Hydrophobic Sols by Non-Electrolytes

So far we have only considered electrolytes. Since in electrokinetic phenomena non-electrolytes, especially those which are capillary-active, sometimes exert an influence (see p. 263), it is possible that they might also be of importance to flocculation. This is indeed the case, although non-electrolytes by themselves do not in general appreciably change the stability of hydrophobic sols. Thus an As_2S_3 sol was not altered after standing many days in the presence of methyl and ethyl alcohols, formaldehyde, ether, acetone, cane sugar, urea, and phenol in large concentrations.[3] The

[1] Journ. Chem. Soc. **67**, 67 *et seq.* (1895).
[2] Zeitschr. f. physik. Chemie, **86**, 458 (1914).
[3] *Freundlich*, Zeitschr. f. physik. Chemie, **44**, 136 (1903).

same result was found for Congo-rubin,[1] a sol of a very different kind.

But flocculation by electrolytes is very distinctly influenced by non-electrolytes. Unfortunately no measurements are as yet available of the influence of non-electrolytes on the velocity of the coagulation caused by electrolytes. All data have been collected for flocculation values. The relationships appear to be fairly simple for Fe_2O_3 sols.[2] Many capillary-active non-electrolytes, such as urethane, camphor, and thymol, depress the F.V. considerably, and thus favour coagulation, a phenomenon that may be described as *sensitization*. While, for example, the F.V. of a pure Fe_2O_3 sol for NaCl amounted to about 35 millimols, it sank to 27 when camphor in a concentration of about 10 millimols per litre was present; it sank to 20 with thymol of about 5 millimols per litre. With the urethanes the sensitizing action increased in ascending the homologous series according to Traube's rule, approximately also quantitatively; the concentration just necessary to produce a certain sensitization decreases for the next higher member of the homologous series to about half. A sensitization of this kind is most likely the cause of the great coarsening produced in the particles of an amicronic gold sol (prepared by the formaldehyde method) by strophanthin, a capillary-active non-electrolyte.[3]

Rona and György [4] could also accelerate the settlement of kaolin suspensions by addition of organic substances such as camphor, thymol, tributyrin, and others, and found an enhanced action in ascending a homologous series. This must certainly be regarded as a sensitization, for the charge on the kaolin particles, which settle freely, may be assumed to be below the first critical potential from the outset. With charcoal suspensions, the particles of which are only feebly charged (see p. 212), such organic substances had no similar influence.

This sensitization may probably be explained as follows. The non-electrolytes are adsorbed by the colloid particles. It has indeed not been possible to prove this directly, probably because with the dilute Fe_2O_3 sols used the quantity of adsorbent was too small; since the content of non-electrolyte in the solution was determined after coagulation, it is also possible that a reversal of adsorption took place, by which the adsorption itself was obscured. If we assume an adsorption at the interface, the dielectric constant there will be distinctly lowered, since all the non-electrolytes have a decidedly lower dielectric constant than water (5 to 20 as against 81). Now Wo. Ostwald [5] has already pointed out that non-electrolytes must also influence the stability of a sol, since the change in the dielectric constant influences the charge. According to equation (2), p. 392,

$$e = \frac{\zeta D r(r + \delta)}{\delta}.$$

Hence if the dielectric constant D is smaller, then e' is also smaller, and a smaller amount of the effective ion adsorbed is necessary in order to pass beyond the first critical charge which leads to slow coagulation; the F.V. must therefore be smaller, and we have a sensitization.

[1] *Wo. Ostwald*, Kolloidchem. Beih. **10**, 204 (1919); further references are given by *Kruyt* and *van Duin*, Kolloidchem. Beih. **5**, 270 (1914).
[2] *Freundlich* and *Rona*, Biochem. Zeitschr. **81**, 87 (1917).
[3] *Pietrkowski*, Biochem. Zeitschr. **98**, 92 (1919).
[4] Biochem. Zeitschr. **105**, 133 (1920).
[5] "Grundriss der Kolloidchemie," 1 Aufl. 1909, p. 441.

If this view is correct, these capillary-active non-electrolytes should also reduce the kataphoretic migration velocity of the Fe_2O_3 sol, for according to equation (8), p. 244,

$$u = \frac{\zeta HD}{4\pi\eta}.$$

A smaller D means a smaller u. Now this was actually the case. While the pure Fe_2O_3 sol had a $u = 0{\cdot}4 \times 10^{-4}$ cm. per sec. for 1 volt per cm., for a sol containing about 5 millimols of camphor $u = 0{\cdot}2 \times 10^{-4}$, and for one with about 2·3 millimols of thymol, $u = 0{\cdot}3 \times 10^{-4}$ cm. per sec.

We might still investigate whether non-electrolytes alone are able to depress the charge of the micellæ below the first critical limit, and whether they do not then cause flocculation. If this should not be the case, the question would have to be asked why the presence of the active ion is necessary in addition to the non-electrolyte.

It must further be noted that the sensitization only appears distinctly in the case of the weakly coagulating univalent inorganic anions, hardly or not at all with the strongly flocculating organic and multivalent anions. This depends upon the shape of the adsorption isothermal. We see from Fig. 113 that, when the adsorbed amounts required for flocculation fall on account of sensitization from a to a', this produces for weakly adsorbed ions, to which the flatter curve refers, a great change from c to c', but only a small one in the case of strongly adsorbed ions, to which the steeper curve refers. A quite similar argument holds on passing from a univalent to a multivalent ion. Here it will of course again be presupposed that what was deduced (see p. 424) for the equilibrium concentration in the solution after adsorption remains valid for the F.V.

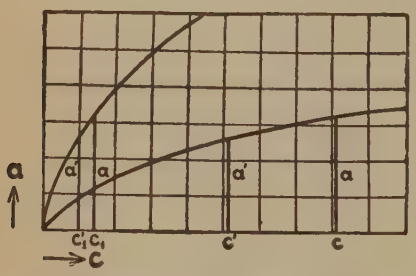

Fig. 113.—Dependence of Sensitization by Non-electrolytes upon Adsorbability of the Coagulating Ion.

With this the multiplicity of the influence of non-electrolytes is not exhausted. Even before the above-discussed sensitization became known, Kruyt and van Duin [1] had pointed out a peculiar change in the F.V. of As_2S_3 sols due to capillary-active substances such as amyl alcohol and phenol. They observed in the flocculation by uni- and tervalent kations a depression of the F.V., a sensitization therefore; with bi- and quadrivalent ions, on the other hand, a rise in the F.V., and hence a check to flocculation. This behaviour is at present difficult to explain. It is, however, quite possible that flocculation is checked by non-electrolytes; they may on account of their own adsorption depress that of the active ion, by displacing it from the interface (see p. 206). A greater concentration, and thus a higher F.V., would be necessary to induce flocculation. But how displacement and sensitization are interconnected in such a way that a particular influence of the valency of the ion is thereby brought into play, is at present not intelligible. Further progress can here only come through investigations of the action of non-electrolytes upon the C.V., and a more exact knowledge of

[1] Kolloidchem. Beihefte, **5**, 269 (1914).

the influence of non-electrolytes on electrokinetic processes in general; in the first place very hydrophobic sols, such as that of gold, should be tested. That it is a question of the adsorption of the capillary-active substances seems to result from the fact that the influence of isobutyl alcohol, isoamyl alcohol, and phenol on the flocculation of As_2S_3 sols runs parallel to their adsorbability by blood charcoal.[1]

Perhaps this group of still inexplicable influences comprises the fact described by Mukherjee and Sen,[2] that the influence of H_2S upon the stability of As_2S_3 sols is different, according as a uni- or multivalent kation is used for flocculation. Towards univalent kations ($K^{\cdot}$, $NH_4^{\cdot}$) H_2S increases the stability, the flocculation values increase; towards multivalent ions, on the other hand ($Sr^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Th^{\cdot\cdot\cdot\cdot}$), H_2S lowers the stability, the flocculation values decrease.

The Influence of Temperature on the Coagulation Velocity

The influence of temperature upon the velocity of *rapid coagulation* should be contained in formula (1), p. 433:

$$k = 4\pi Dr = \frac{2}{3}\frac{RT}{N}\frac{r}{\eta r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It should be therefore chiefly a matter of the temperature dependence of the viscosity of the dispersion medium, since this has the largest temperature coefficient of all the quantities occurring in the equation. Thorough experiments in this direction have not yet been undertaken, but the general validity of formula (1) for the small range of temperatures hitherto investigated suggests that it will be generally confirmed.[3]

For *slow coagulation* we have equation (3), p. 437:

$$k' = 8\pi Dr\xi = \frac{4}{3}\frac{RTr\xi}{N\eta r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It could be referred back to (1) for rapid coagulation, if ξ, the fraction of effective encounters, were independent of temperature. This is, however, certainly not the case, as already results from experiments by Westgren [4] on coarse gold sols, nor was it to be expected from the considerations on p. 442, since various quantities sensitive to temperature are involved in them. We have therefore to reckon with a particular temperature dependence of slow coagulation, which distinguishes it from rapid coagulation.

The measurements by Westgren above referred to, which were carried out by the reliable method of ultra-microscopic counting, are not extensive enough to allow further conclusions to be drawn. Miyazawa [5] followed the slow flocculation of Al_2O_3 sols at various temperatures by means of the time change of the viscosity; as coagulator sodium mesaconate was used. The dependence upon temperature could be satisfactorily represented by the well-known formula of Arrhenius,[6] which holds so widely for the temperature dependence of chemical reaction. If $\varkappa$ is the C.V. constant, then

$$\log \varkappa = -\frac{A}{T} + B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where A and B are constants. This is seen from Table 125.

[1] *van Duin*, Kolloidzeitschr. **17**, 123 (1915).
[2] *loc. cit.* p. 447.
[3] *Zsigmondy, loc. cit.* p. 431.
[4] *loc. cit.* p. 441.
[5] *loc. cit.* p. 416.
[6] Zeitschr. f. physik. Chemie, **4**, 226 (1889).

TABLE 125

Dependence of the Velocity of Coagulation of Al_2O_3 Sols on Temperature

A = 4,509; B = 10·625

t in deg.	T.	κ (obs.).	κ (calc.).
18	291	0·0077	0·0077
22	295	0·0092	0·0094
24	297	0·0105	0·0105
26	299	0·0122	0·0116
29	302	0·0131	0·0135
32	305	0·0156	0·0156

A value of constant A of about 4,500 corresponds to that frequently found for ordinary chemical reactions; that is to say, for every 10° the velocity is about doubled. The statement of Mukherjee and Papaconstantinou [1] is curious, namely that the C.V. of a gold sol, as followed spectrophotometrically, increases with the temperature when $Sr^{\cdot\cdot}$ and $Ba^{\cdot\cdot}$ ions are used as coagulators, but changes only slightly when $K^{\cdot}$ ions are employed. An observation of Mukherjee's [2] also points to an influence of the valency of the kation on the dependence of the C.V. upon the temperature. Thus with As_2S_3 as sol and $K^{\cdot}$ ions as coagulator, the time necessary for a definite degree of coagulation increases with rise of temperature; with multivalent kations, on the other hand, it decreases. The As_2S_3 sol is however little suited to an investigation of the influence of temperature, because the As_2S_3 suffers an hydrolysis which is certainly perceptibly sensitive to temperature, and H_2S also influences the stability of the sol.

The dependence of the *reversal of adsorption*, and hence of the coarsening of fresh flocculi, upon temperature may likewise be represented by equation (3), as Table 126 shows. This deals with HgS flocculi, flocculated from an HgS sol by new fuchsine.[3]

Here the constant A is far greater, the velocity increases about fourfold or a rise of 10°.

TABLE 126

Dependence of the Velocity of the Reversal of Adsorption upon Temperature

A = 13,925; B = 33·09

t in deg.	T.	$\kappa \cdot 10^6$ (obs.).	$\kappa \cdot 10^6$ (calc.).
0·2	273·2	0·017	0·017
25	298	1·3	1·2
35	308	4·7	5·4

That the dependence of flocculation upon temperature so frequently closely resembles that of the velocity of chemical reactions, is intelligible

[1] Journ. Chem. Soc. **117**, 1563 (1920).
[2] Journ. Chem. Soc. **117**, 350 (1920).
[3] *Freundlich* and *Schucht*, *loc. cit.* p. 453.

according to the considerations on p. 434. Both phenomena are in so far similar to one another, that in the one case it is a matter of the collision of micellæ, in the other of molecules, and only a fraction of the encounters is effective.

It may now be noted, as will be discussed more in detail later (p. 474), that the foregoing considerations only apply when it is not necessary to reckon with a peptizing influence acting at the same time as the coagulating influence. With the former rise of temperature favours peptization and hence hinders coagulation. A higher concentration of coagulator may then sometimes be necessary, in order to attain the same C.V. The F.V. increases with the temperature, and does not sink, as should be the case if the C.V. is increased by rise of temperature. This was observed for example by Wo. Ostwald [1] with a Congorubin sol, the influence of temperature being so considerable that work was best carried on in a thermostat, whereas with most other sols the F.V.'s can be measured with so little exactitude, that the errors due to inconstancy of temperature may be neglected.

Sols behave very differently upon simple warming, even without addition of a coagulator. Many, such as the numerous sulphides (As_2S_3,[2] Au_2S_2 [3]), hydroxides (Fe_2O_3 [4] and others), metals (gold sols in alkaline solution [5] and others) bear long-continued boiling without flocculating ; others, as in particular many metallic sols, e.g. that of Pt, coagulate quickly upon warming.[6] The dependence of the C.V. upon temperature has here probably only little influence, the most essential thing being chemical changes, which displace the equilibrium between the micellæ and the electrolyte of the intermicellar liquid. According to Kruyt and van der Spek [7] boiling an As_2S_3 sol causes above all a coarsening of its particles. Hence the flocculation values measured upon the boiled and cooled sol differ from those for the unboiled sol in the same way as do those of a dilute sol from those of a concentrated one. The number of particles and the interfacial area have become smaller. As in the former case (cf. p. 448) with $K^{\cdot}$ ions the influence of the decreased frequency of the encounters resulted in an increase of F.V. for the diluted sol, so also in the case of the boiled sol. With bi- and ter-valent kations on the contrary the influence of diminished adsorption at the smaller interface preponderates and causes a decrease in F.V.

The Heat of Flocculation of Lyophobic Sols

The heat of flocculation of hydrophobic sols is very small. Careful calorimetric measurements on As_2S_3 and Fe_2O_3 sols were undertaken by Kruyt and van der Spek,[8] after Linder and Picton [9] had already carried out such experiments with an As_2S_3 sol, and Doerinkel [10] with Fe_2O_3 and Ag sols. Kruyt and van der Spek found for As_2S_3 sols a heat evolution of 0·01 to 0·05 gram-calories per gram of As_2S_3, and for Fe_2O_3 sols a positive heat change of 2 calories per gram of Fe_2O_3.

[1] *loc. cit.* p. 416.
[2] *H. Schulze*, Journ. f. prakt. Chemie, **25**, 437 (1882).
[3] *E. A. Schneider*, Ber. d. deutsch. chem. Ges., **24**, 2244 (1891).
[4] *Geffcken*, Zeitschr. f. physik. Chemie, **49**, 298 (1904).
[5] *Zsigmondy*, Lieb. Ann., **301**, 32 (1898).
[6] *Bredig* and *Müller v. Berneck*, Zeitschr. f. physik. Chemie, **31**, 321 (1899).
[7] *loc. cit.* p. 447.
[8] Kolloidzeitschr. **24**, 145 (1919).
[9] Journ. Chem. Soc., **61**, 144, 146 and 153 (1892).
[10] Zeitschr. f. anorg. Chemie, **66**, 20 (1910) ; **67**, 161 (1910).

These small heats of flocculation agree entirely with other experiences with lyophobic sols. Adsorption in solutions has usually a small temperature coefficient and hence a small latent heat (cf. p. 225). With flocculation the amount of effective ion adsorbed is small, the heat of adsorption is therefore not great, and it becomes still smaller since we are dealing with an exchange adsorption, another ion passing from micella into the solution to replace the effective one; this process causes a heat change of opposite sign. The heat change resulting from the diminution in surface area of the colloid particles can only be insignificant. In coagulation itself only a very slight decrease in surface takes place, since the particles adhere to one another but do not coalesce (cf. p. 472). The greatest share in the heat of flocculation is indeed taken by the heat change caused by the dehydration or hydration of the colloid particles which accompanies flocculation, that is, by the passage of water in either direction between micella and intermicellar liquid. Hence it comes about that the somewhat hydrophilic Fe_2O_3 sol has a considerably greater heat of flocculation than the more hydrophobic As_2S_3 sol. With true hydrophilic sols we then meet with heats of coagulation considerably greater (cf. p. 627).

Linder and Picton[1] investigated the change in volume of sols upon flocculation by means of a sensitive dilatometer; this was so constructed that by simple inclination the coagulating electrolyte could be introduced and then effectively stirred. With an As_2S_3 sol the volume changed upon flocculation by the same amount, within the limits of error, as upon dilution with pure water; the volume change was practically zero. With a Fe_2O_3 sol, on the other hand, flocculation was accompanied by a small dilatation of the solution, which certainly exceeded the limits of error; the formation of the sol is thus accompanied by a contraction. Fe_2O_3 sols thus certainly more nearly resemble hydrophilic sols in this respect.

The Bearing of Flocculation upon other Processes

There are a large number of processes in technology and in the phenomena of living beings which are unquestionably closely connected with flocculation. It is true that we cannot always tell whether it is actually a matter of flocculation, or whether more directly the influence of electrolytes upon electrokinetic processes; in both cases we have the strong influence of adsorbability and valency.

Upon coagulation depends the use of salts of iron, aluminium, and other kations of high valency in the clarification of effluents. That sewage is rich in negative colloids was proved by W. Biltz and Kröhnke.[2] It is probable that these colloids are partly hydrophobic. The powerful effect of tervalent kations is thus explained. Many other kinds of turbidity may also, if negative, be cleared up by means of kations of high valency, or, if positive, by anions of high valency. Aluminium sulphate or alum is a particularly suitable coagulator for this purpose, since it contains a tervalent kation and a bivalent anion. A powerful action may be expected without its being necessary to determine the charge of the suspended particles. It should be noted that with tervalent kations irregular series may occur; the concentration of the coagulator must not therefore be chosen too high, and must be altered according to the conditions of experiment.

[1] Journ. Chem. Soc., **67**, 72 (1895); **87**, 1907 and 1923 (1905).
[2] Ber. d. deutsch. Chem. Ges., **37**, 1745 (1904).

The following phenomenon was quite rightly referred by Reichert [1] to flocculation. The flagella of many bacteria are so fine that they are not immediately visible under the microscope. They become so, however, in solutions of electrolytes; and if the concentration necessary to produce visibility be determined, a strong dependence upon the nature of the kation is found. With light metal kations those of the same valency in equivalent concentrations have an equally strong, those of different valency a widely divergent effect, the concentration required being always smaller for those of higher valency; heavy metal kations require a lower concentration than corresponds with their valency, and so on. It is a matter of several flagella having to combine to form a tuft before they are thick enough to be visible. For the association of these ultramicroscopic flagella to form coarser tufts the same circumstances obviously play a part as in the coagulation of negative colloid particles to coarser flocculi. If at any time peculiarities in the flocculation of rod-shaped particles should appear, one would expect to meet them in the case of these flagella also.

More uncertain and difficult to explain are the phenomena of excitation and of toxicating and detoxicating influences, such as are described by J. Loeb and Lillie and their co-workers. It is here always a matter of mixtures of electrolytes. The valency of the kation scomes in. But still more striking is the antagonism between various kations, such as has already been mentioned in the case of more hydrophilic sols (p. 461). As an example the following may be taken.[2] The cilia of the larva of an annelid (Arenicola) are rapidly liquefied and destroyed by sodium ions. Other kations act as antidotes, the minimum concentrations necessary in the case of bivalent kations of the light metals lying between 1 and 10 millimol per litre, of tervalent between 0·01 and 0·1 millimol. Heavy metal kations again act more strongly than corresponds to their valency. The lyotropic order of the kations is also pronounced. In any case this also suggests that we are dealing with changes in colloids which are not strictly hydrophobic, but approach the hydrophilic colloids, in which therefore the influence of hydration is strongly marked. Indeed, the relationships rather resemble those of the hydrophilic sols, such as Odén's sulphur sols or the lecithin sols, to be discussed later. They will therefore be discussed more in detail in that connexion (cf. p. 620).

In biological and physiological literature statements are frequently met with concerning the flocculating action of non-electrolytes which are at first surprising. Now the judgment of such phenomena is rendered more difficult by the fact that we do not know to what extent the colloids in question are hydrophilic rather than hydrophobic.[3] But the possibility must always be taken into account that we are dealing with a sensitization. We are certainly justified in doing so, since electrolytes are always present in the cell in such concentrations, that the flocculation of a hydrophobic sol may occur, particularly if sensitized by a capillary active non-electrolyte. The following are probably cases of this kind. According to O. Warburg and Wiesel [4] a flocculation is produced in yeast press-juice by members of the alcohol, urethane, nitrile, and ketone series, and this power increases decidedly

[1] Zentralbl. f. Bakteriol. Abt. I, **51**, I (1909).

[2] *Lillie*, Amer. Journ. of Physiol. **10**, 433 (1904).

[3] That capillary active substances may also sensitize hydrophilic sols is perhaps to be concluded from a statement of *Hardy's* [Journ. of Physiol. **33**, 290 (1905)] that an alkali globulin sol goes to a jelly upon addition of camphor.

[4] Pflüg. Archiv, **144**, 465 (1912).

with rise in the homologous series. Meyerhof [1] rendered the supposition of a sensitization very probable by the following experiment. If the disperse phase of the press-juice is filtered off by means of an ultra-filter, washed out and repeptized, its coagulation is not sensitized by addition of urethane, but this happens when the intermicellar liquid, originally filtered off, is added. The electrolytes contained in the intermicellar liquid are required to render possible the sensitization by urethane. The observation of Battelli and L. Stern [2] that narcotically active alcohols and ketones produce flocculation in solutions of nucleoproteins is probably another example.

The following circumstance pointed out by Meyerhof is perhaps important for the theory of the influence of non-electrolytes upon electrokinetic phenomena and in sensitization. The adsorption isothermal does not always hold for the action of organic substances, but in the cases of sensitization, coagulation of yeast press-juice, and in other cases, we have a linear dependence upon the concentration of the organic substance or even one convex to the axis of concentration. The circumstance possibly takes effect here that a displacement of the active electrolyte by the organic substance preponderates more strongly than the depression of the charge under the influence of the dielectric constant.

Whether the widespread occurrence of autocatalytic processes in nature may be connected with the autocatalytic course frequently observed in connexion with coagulation and reversal of adsorption, will be better discussed later (p. 752).

The Peptization of Coagulated Flocculi of Hydrophobic Sols

By peptization we understand, as already mentioned, the phenomenon of the bringing into colloidal solution, by suitable means, of the coagulated flocculi of a sol or, more generally, of a given solid body. Quantitative methods of following peptization have not yet been worked out. One might imagine the possibility of determining under definite conditions of stirring, etc., the velocity with which particles of a given maximum size are formed; this size might be limited by the possibility of filtration through suitable ultra-filters. Some qualitative results are available concerning the behaviour of flocculi of hydroxide sols coagulated by electrolytes. The powdery particles which are formed by the flocculation of sols of the metals such as gold, silver, platinum, can rarely be peptized by washing out with pure water or aqueous solutions. Those exceptions which occur appear to depend upon the presence of organic substances; and curiously enough it is, in two cases, the same chemical substance, namely citric acid (or the citrate ion) or another citrate compound. Thus the disperse phases of a Carey Lea [3] silver sol (prepared by the interaction of silver nitrate and ferrous citrate) and of Nordlund's [4] mercury sols containing potassium citrate, may be repeptized. Derivatives of citric acid, such as the sodium salt of anhydromethylenecitric acid (which appears in commerce as "Citarin") [5] are also effective. The flocculi which have

[1] Biochem. Zeitschr. **86**, 325 (1918). He did not use the same juice as *Warburg* and *Wiesel*, but a juice produced by maceration (*Lebedew*); this is, however, closely allied to the pressed juice, and also shows in particular the flocculation by organic liquids.

[2] Biochem. Zeitschr. **52**, 226 and 253 (1913); cf. also *Meyerhof*, Pflüg. Archiv, **157**, 251 (1914).

[3] *loc. cit.* p. 386.

[4] *loc. cit.* p. 403.

[5] *Vanino*, Kolloidzeitschr. **20**, 122 (1917).

been coagulated from sulphide sols are on the whole more easily peptized, particularly by means of water containing H_2S.

The smooth peptizability of Congorubin is very striking; a sol which has been turned blue by a neutral salt or by an acid again becomes red when diluted with a suitable amount of water.[1] A similar phenomenon is the decrease in course of time of the double refraction of a V_2O_5 or a benzopurpurin sol (cf. p. 414), which immediately after dilution is still very strong.

Best known is the peptization of the flocculi of hydroxide sols. Linder and Picton [2] carried out experiments on Fe_2O_3 flocculi, Freundlich and Leonhardt [3] on flocculi of V_2O_5 and Mo_2O_5. They may all be brought into colloidal solution again by washing out with water. In every case it is of advantage if as short a time as possible is allowed to elapse between flocculation and peptization. Peptization also depends greatly upon the nature of the ion which has been mainly active in flocculation. Flocculi which have been coagulated with weakly coagulating ions—the univalent inorganic anions with the positive Fe_2O_3 sols, the univalent inorganic kations with the negative V_2O_5 and Mo_2O_5 sols—may be readily and smoothly peptized by washing out with water. It becomes increasingly more difficult the more strongly coagulating the ions were, hence with strongly adsorbed ions and ions of high valency. Table 127 gives a semi-quantitative picture of this behaviour; the experiments contained in it were carried out as follows. The sol was flocculated with electrolyte solution, quickly centrifuged, and the supernatant liquid decanted from the flocculi. The latter were then stirred with a definite volume of water. If they remained peptized, the table states "coagulum peptized by first digestion"; if this did not happen, centrifuging was again performed, and it was then noted whether peptization occurred on addition of fresh water to the flocculi. This was repeated until peptization, which, in many cases, was only slight, was observed.

TABLE 127

Peptization of Flakes of a Mo_2O_5 Sol coagulated by various Electrolytes

Coagulator.	Peptization at 18° to 20°.
NaCl	Coagulum completely peptized during 1st digestion
NH_4Cl	" " " " 1st "
KCl	" " " " 2nd "
Aniline sulphate	" " " " 1st "
Guanidine nitrate	" " " " 2nd "
Morphine hydrochloride	" " " " 3rd "
$\frac{Tl_2SO_4}{2}$	" slightly " " 7th "
$Sr(NO_3)_2$	" completely " " 6th "
$BaCl_2$ [4]	" slightly " " 7th "
$\frac{Al_2(SO_4)_3}{2}$	" " " " 7th "
$Ce(NO_3)_3$	" " " " 7th "

[1] *Wo. Ostwald*, Kolloidchem. Beiheft. **10**, 226 *et seq.* (1919).

[2] Journ. Chem. Soc. **87**, 1926 *et seq.* (1905).

[3] *loc. cit.* p. 451.

[4] The F.V. of $Sr(NO_3)_2$ and $BaCl_2$ was distinctly different ($Sr(NO_3)_2$ 0·61 millimol, $BaCl_2$ 0·19).

This behaviour may be satisfactorily explained from the structure of the coagulated flocculi and the properties of the velocity of coarsening.[1] When during coagulation single particles associate to double and multiple ones, it does not signify that they cease to exist as individual particles and forthwith coalesce rapidly. The contrary is, as we know, the case. Much experience (cf. p. 454) goes to show that, not only when they are solid amorphous, but even when they are liquid, they continue to exist for a longer or shorter time as individual particles associated together as larger flocculi. Only a few examples will be given. On p. 344 it was mentioned that in faintly acid solutions the gamboge and mastic particles of the corresponding emulsions arrange themselves without coalescing in rows upon the wall and so allow their diameter to be measured. Powis [2] describes the same phenomenon in the coagulation of oil emulsions, a particularly important case, since we are actually dealing with drops of liquid. Here also, under the ultramicroscope, the original single particles are recognizable as such in the flocculi resulting from coagulation. This is particularly clear, for example, with the rod-shaped particles of a V_2O_5 sol; one finds that the flocculi sometimes arrange themselves in rows and still perform oscillations singly. Bundle-like heaps may also be recognized. As Zsigmondy [3] points out, ultramicroscopic films of liquid are retained between the particles.

The flocculating electrolyte is removed by washing out. As soon as so small a concentration is thereby attained as to cause a decided charging up of the micellæ, in that range of the ζ, c curve, therefore, which corresponds to the maximum (the piece ABC of curve 2, Fig. 50, p. 259), the diffuse double layer is again completely formed upon the particles in the extremely thin layer of liquid which still separates them. It is naturally also possible that other electrolytes originally contained in the micella produce the charge. The formation of the double layer opposes the attraction of the particles, exactly as it originally stood in the way of their association (cf. p. 432). The single particles contained in the flocculi separate, the attraction becomes less effective, the molecular motion gets the upper hand and tears the particles out of the association of the flocculi.

In many cases the washing out of the electrolyte does not alone suffice: it may be that in small concentrations it does not communicate a sufficient charge, or that the micella contains no other residues of electrolyte which can act in this sense. Other electrolytes which have a high and extended maximum of the ζ, c curve must then be added. The OH' ion, which is particularly conspicuous in this respect, is therefore, in the case of particles which take a negative charge, a highly successful peptizing agent. A little alkali is added to the water when it is desired to disperse metals colloidally by electrical disintegration (cf. p. 509). According to Whitney and Blake,[4] coagulated gold particles may be successfully peptized by a little ammonia. The citrate ion is also very active in the same sense (see p. 470). Sulphide particles are frequently peptized by sulphuretted hydrogen or alkali sulphides.[5] Just as the OH' ion is a powerful peptizing agent for negative particles, so is the H' ion for positive particles. A. Mayer, Schaeffer and Terroine [6] describe the following experiment. Under the ultramicroscope

[1] See in particular *Zsigmondy*, Zeitschr. f. anorg. Chem. **89**, 210 (1914).
[2] Zeitschr. f. physik. Chemie, **89**, 194 (1915).
[3] *loc. cit.* p. 454.
[4] Journ. Amer. Chem. Soc. **26**, 134 (1904).
[5] *Linder* and *Picton*, Journ. Chem. Soc. **61**, 114 (1892).
[6] Compt. rend. **145**, 918 (1907).

the amicrons of a Fe_2O_3 sol were coagulated by alkali to submicrons; by addition of acid these submicrons could again be split up into amicrons.

That the ion active in flocculation plays so important a part in peptization has the following cause. The coarsening of the flocculi has a great similarity with coagulation; it is therefore to be expected that the ions which flocculate strongly in small concentrations will also strongly favour coarsening. Even appearances favour this view. Both in the case of an As_2S_3 sol, as also of Mo_2O_5 and V_2O_5 sols, the flocculi which have been coagulated by univalent inorganic kations are much looser or more jelly-like than those produced by multivalent or strongly adsorbed ions.[1] We are therefore justified in believing that the particles of the flocculi formed by the weakly coagulating ions have coalesced far less than those formed by strongly coagulating ions; the loose flocculi contain far more dividing liquid than the denser ones. The peptization of the denser flocculi must therefore be correspondingly more difficult.

A second circumstance must be added. It was pointed out on p. 263 how, in consequence of the form of the adsorption isothermal, the feebly adsorbed ions may easily be washed away from a boundary surface, the strongly adsorbed ones with difficulty. This must also be of influence here; the difficulty in removing the strongly adsorbed ions completely and quickly hinders an effective production of charge.

Finally, the following must also be considered. Powis[2] points out how, for the ease of peptization of sols coagulated by univalent inorganic ions, the fact is important that, for example, with As_2S_3 sols a higher charge remains in the particles when $K^{\cdot}$ ions are used for coagulation than when multivalent kations are employed (cf. p. 419). A higher charge at the commencement facilitates the reattainment of the originally higher charge. In general, the hydration influences frequently discussed (cf. p. 462) will also be of very decided importance for peptization.

The influence of temperature upon peptization cannot yet be definitely described. The rate of coarsening frequently has a large temperature coefficient (cf. p. 466). Hence we might expect that flocculi produced and maintained at a lower temperature would coarsen more slowly, and therefore peptize more readily, than those produced at a higher temperature. This is apparently the case from some experiments by Freundlich and Leonhardt on Mo_2O_5 sols; at 0–2° the flocculi were much more easily peptized than at 18–20°. On the other hand, Wo. Ostwald[3] describes the following phenomenon: a Congorubin sol turned blue by addition of electrolyte again becomes red, and is therefore peptized, on warming, while upon cooling it once more assumes the blue colour. Here therefore rise of temperature appears to favour smoothly and reversibly the dispersion of the flocculi, and lowering of temperature to produce a coarsening. Perhaps the difference depends upon the fact that in the case of a Congorubin sol only a few micellæ have associated to quite small flocculi, while in the case of a Mo_2O_5 sol the separated flocculi contain many micellæ which

[1] This behaviour apparently does not hold generally. With a Congorubin sol [*Wo. Ostwald*, Kolloidchem. Beiheft. **10**, 228 (1919)] the coagulum produced by acids is much looser than that produced by neutral salts, although the acids have smaller flocculation values. Perhaps this is due to the circumstance that the acid coagulum contains Congorubinic acid, and therefore differs more from the flocculi obtained with neutral salts than is the case with many other sols.

[2] *loc. cit.* p. 419.

[3] Kolloidchem. Beiheft. **10**, 230 *et seq.* (1919).

coarsen to much denser and larger grains. As already mentioned above (p. 467), this behaviour of a Congorubin sol towards changes of temperature is responsible for the fact that its flocculation values rise with temperature.

Liquids and solids in mass are more difficult to peptize by suitable electrolytes. The process does not take place spontaneously. On the contrary, it is necessary mechanically to divide up the liquid or solid mass very finely, in order that the charging action of the peptizing ion may become effective. In the case of liquids it is often sufficient to emulsify them by energetic stirring and to employ as peptizing agent OH' ions in aqueous solution, provided that the liquid has the tendency to take a negative charge. The OH'-ion concentration must be chosen sufficiently small since larger concentrations fall outside the maximum of the ζ, c curve, and the OH' ion again has a flocculating action. Whitney and Straw [1] compared the most favourable concentrations for this peptizing influence of the OH' ion in the case of liquids such as turpentine, carvone, and carvene, of solids such as soot and kaolin, and in the production of a colloidal silver solution by the method of electrical disintegration (cf. p. 509). The most favourable concentrations varied between 0·2 and 80 millimols per litre, a range which does not appear considerable for such diverse substances. This speaks in favour of the view that the extent of the maximum of the ζ, c curve alters comparatively little with the nature of the liquid and solid substances.

Gengou[2] has also closely examined the peptizing influence of citrate ions upon various solids (charcoal, clay, kaolin, ZnS, $BaSO_4$, etc.). He measured the adsorption upon $BaSO_4$, for which the isothermal holds, the displacing action of the adsorption of other substances, of dyes, etc.

Also in the preparation of mercury sols, which may be effected either by mechanical shaking, by condensation of the vapour or by electrical disintegration (cf. p. 403), potassium citrate proved to be a particularly effective peptizing agent; the optimum lay at about 0·8 millimol per litre.

One is inclined to attribute this power of the citrate ion to its tervalency. But there are also univalent organic ions which are remarkable in this respect. Thus, the picrate ion appears to have a particularly high maximum of the ζ, c curve and so to peptize easily. With its aid, blood charcoal may be suspended, a maximum effect occurring, as always, at a certain concentration.[3] The picrate ion is possibly strongly electrotonic (cf. p. 423), and this is perhaps the reason for its peculiar behaviour in so many respects. For it does not depend upon a particularly strong adsorbability; many anions (salicylate and others) are more strongly adsorbed without their showing such a striking power of peptization. The same holds for the anions of some organic sulphonic acids, which peptize strongly and yet are but slightly adsorbed.

If solid bodies are not originally fine-grained, as in the case of soot or kaolin, they must be carefully powdered if we desire to peptize them.[4]

[1] Journ. Amer. Chem. Soc. **29**, 325 (1907).

[2] Arch. internat. d. physiol. **7**, 57 (1908); see also *Brossa* and *Freundlich*, Zeitschr. f. physik. Chemie, **89**, 328 (1915).

[3] *Freundlich*, Zeitschr. f. physik. Chemie, **57**, 462 (1907).

[4] *Plauson* [Chem.-Ztg. **44**, 553, 565 (1920); Zeitschr. f. angew. Chem. **34**, 469, 473 (1921)] has recently described a so-called colloid mill, a mechanical arrangement for colloidally dispersing solids and peptizing them; a percussion (hammer and anvil) mill is used and grinding is performed in presence of the dispersion medium.

The diameter of the particles must not be greater than 1μ. This is the size at which molecular motion and increase in solubility in consequence of decreased radius of curvature become noticeable.[1] Mechanical pulverization can further be assisted by chemical action, if this so roughens the surface of the solid that the small particles of it are charged up further by peptizing influences and torn off. Upon this depend in part the methods in which solid substances can be peptized by alternate attack with acids and alkalis or with other reagents (cf. p. 514).

Up to the present the point of view has been taken that the charging effect of the ions, as expressed by the maximum of the ζ, c curve, is chiefly responsible for the peptizing action. Nordlund[2] describes a curious change produced in the particles of a mercury sol by peptizing electrolytes which almost makes it appear questionable whether peptization can be caused solely by the communication of a charge: mercury sols which contain little or no peptizing electrolyte, such as citrates or ammonium salts, oxidize comparatively rapidly in air; this oxidation is greatly inhibited by the peptizing electrolytes named, indeed, it is apparently completely prevented. One might almost imagine it to be a chemical change, were it not for the fact that the complete occupation of the surface by the electrolytes prevents the adsorption of oxygen, which is probably the preliminary step to an oxidation of the kind. It would then be a question of a phenomenon fundamentally similar to that observed by Marc in the inhibition of crystallization by adsorbed substances (cf. p. 336). The more hydrophilic a sol is, the more will one expect chemical interaction with the solvent, hydration, in connexion with peptization; in short, those influences which determine the formation of the solution molecule of truly dissolved substances.

Peptization in the Thawing of Frozen Sols

The behaviour of the flocculi of lyophobic sols upon freezing and subsequent thawing corresponds to a large extent to the behaviour of flocculi produced by electrolytes. If a sol is allowed to freeze, it becomes in general more concentrated, both as regards electrolytes and other foreign substances. Hence the lower limit of the first critical charge may be passed, and the sol flocculated. It is possible that the original concentration of electrolyte may not suffice for this. It will then only occur in a slight degree, and the colloid particles will remain distributed between the ice crystals as they grow. We must probably always assume, however, that they are more closely packed than in the original sol. Between the more closely packed single particles, or those contained in the flocculi, will be exceedingly fine frozen films of the dispersion medium. But this condition of a fine structure of ice crystals does not correspond to a state of equilibrium. The fine crystals will become coarser, and force out and press together the particles between them, thus favouring their further coalescence. It is the same phenomenon as described on p. 330 in connexion with the subsequent coarsening of melts of benzophenone containing foreign matter, which belongs to the phenomena of coarsening and the reversal of adsorption. The coalescence of the particles and their further coarsening will similarly depend upon the nature and concentration of the elec-

[1] See *v. Weimarn*, Kolloidzeitschr. **4**, 123, 198 (1909).
[2] *loc. cit.* p. 403.

trolytes contained in the sol, as was described under reversal of adsorption (cf. p. 453).

If now the sol is thawed comparatively soon after freezing, that is, at a time when the fine films of ice are still present, the few associated particles will be separated by films of liquid and can be charged and peptized by further melting of the ice and the consequent dilution of the solution. This also holds particularly when no strongly coagulating electrolytes are present. But if the thawing is delayed for some length of time, the particles may be so closely associated as to be no longer peptizable. Sols, the disperse phases of which are easily peptized after flocculation by electrolytes, will also be easily peptized upon thawing, especially if not too long a time has passed since freezing took place.

Experience entirely confirms these expectations. A systematic comparison of peptization after coagulation by electrolytes with that upon thawing is not, it is true, available. But everything favours the view that flocculi, such as those of the metals, which are otherwise difficult to peptize, are also difficult to bring into colloidal solution by thawing, while this takes place much more smoothly with the easily peptizable flocculi of hydroxide sols.[1] The otherwise easily peptizable silver sol of Carey Lea is also comparatively easily peptized upon thawing.[2] It also holds in general, that one is more likely to obtain a sol again if thawing takes place soon after freezing than if one waits for a longer time.[3] If in analytical work it is required to make the particles of a colloidal solution coarser and easier to filter, this may frequently be attained by complete freezing and thawing.[4]

The statement[5] is frequently found that electrolytes are necessary to re-peptize the flocculi separated by freezing. This probably depends in the first place upon the fact that with sols very poor in electrolytes the quantity of electrolyte present does not suffice to re-charge the flocculi sufficiently. Further, the statements in question deal in part with sols with comparatively large amounts of electrolyte and small amounts of the disperse phase (e.g. Fe_2O_3 sols not dialysed, or selenium sols with excess of selenious acid). Such sols are indeed much more allied to the hydrophilic sols, and questions of hydration sensibly affect their behaviour.

The Interaction of two Lyophobic Sols

If two sols, the micellæ of which have a different chemical composition but the *same* sign of charge, are mixed, in the majority of cases no striking change is produced. It has been recently observed, however,[6]

[1] *Ljubawin*, Journ. d. russ. phys.-chem. Ges. **21**, 397 (1889), cited from Ber. d. deutsch. chem. Ges. Referat. **22**, 727 (1889); *E. A. Schneider*, Ber. d. deutsch. chem. Ges. **24**, 2242 (1891); *Linder* and *Picton*, Journ. Chem. Soc. **67**, 73 (1895); *Bredig*, "Anorgan. Ferm." p. 28 (1901); *Gutbier*, Zeitschr. f. anorg. Chemie, **32**, 292 (1902); particularly *Lottermoser*, Zeitschr. f. physik. Chemie, **60**, 462 (1907); Ber. d. deutsch. chem. Ges. **41**, 3976 (1908); *Bobertag*, *Feist* and *H. W. Fischer*, *ibid.* **41**, 3675 (1908); *Gutbier* and *Flury*, *ibid.* **41**, 4259 (1908).

[2] *Prange*, Rec. d. trav. chim. d. Pays-Bas, **9**, 126 (1900).

[3] *Lottermoser*, Ber. d. deutsch. chem. Ges. **41**, 3976 (1908); *Bredig* and *A. Marck*, *van Bemmelen*-Festschrift, p. 345 (1910); *R. Emslander*, "Der Einfluss des Gefrierens auf Selenhydrosole." Diss., Stuttgart, 1913, p. 21.

[4] *Gutbier* and *Flury*, Ber. d. deutsch. chem. Ges. **41**, 4260 (1908).

[5] E.g. *Lottermoser*, *Gutbier* and *Flury*, *loc. cit.* under [3]; *R. Emslander*, *loc. cit.* under [3].

[6] *Freundlich* and *Nathansohn*, Kolloidzeitschr. **28**, 258 (1921).

that a negative As_2S_3 sol is rendered turbid and flocculated by an amicronic Odén sulphur sol, which is likewise negatively charged, and that the flocculation values of the mixed sols are lower than those of the pure ones. This is probably a special case, and not an example of general behaviour. As will be discussed later (cf. p. 618), the presence of a small amount of pentathionic acid is necessary for the stability of the sulphur sol. This is, however, decomposed by sulphuretted hydrogen (cf. p. 619) which is contained in certain amounts in the As_2S_3 sol in consequence of hydrolysis alone. It is the interaction between this H_2S and the pentathionic acid of the sulphur sol which alters the conditions of stability of the mixed sols.

It must, however, be noted that there are cases in which similarly charged particles certainly unite. This is true in the first place for every sol which has been coagulated by an electrolyte and whose particles still carry charges below the first critical potential. It is further known that the particles of a gold sol are also adsorbed by amphoteric, or weakly negative, adsorbents, such as animal charcoal.[1]

Concerning sols of different kinds with particles of like charge, which are *not* coagulated on mixing, the following must be noted. The flocculi which appear upon the coagulation by electrolytes of such a mixed sol, contain, as far as experience hitherto goes, single particles of both sols. It is true that the experiments are not sufficiently exhaustive to decide whether under certain circumstances a separation of the particles may not occur through coagulation. If this is not the case, it confirms the experimental fact that the charge of micelæ of different chemical composition is originally only slightly different (cf. p. 392); it would further indicate that the particles do not differ greatly as regards their adsorptive power for the effective ion.

Upon this joint flocculation of similarly charged particles depends the fact, well known in analytical chemistry, that the metallic hydroxides have a strong tendency to separate out together and that one hydroxide carries another down with it under conditions in which it would otherwise remain in solution.

Better known are the phenomena which are observed when two sols with *oppositely charged* particles are mixed together. They have been especially investigated by W. Biltz.[2] If the particles of one of the sols are in decided excess, no flocculation occurs. The sol has the colour and properties of the colloid whose particles are in excess, although it appears more turbid. The particles of the sol present in excess cover those of the other. This appears, for example, in the fact that in kataphoresis all particles migrate towards that pole whose charge is opposite in sign to that of the particles of the sol present in excess. L. Michaelis and Pincussohn[3] were able to make this behaviour directly visible by mixing a mastic emulsion with an indophenone suspension. The mastic particles appear white, the indophenone particles red. When mastic was added in excess to indophenone, only white particles could be seen in the ultramicroscope.

Between the two limiting cases, in which one sol or the other is in decided excess, there is an intermediate region, in which mixing com-

[1] *Zsigmondy*, Kolloidchemie, 3rd Ed., 1920, p. 94.

[2] Ber. d. deutsch. chem. Ges. **37**, 1095 (1904); then also *Neisser* and *U. Friedemann*, *loc. cit.* p. 429.

[3] Biochem. Zeitschr. **2**, 251 (1906–07).

pletely or partially flocculates both sols. Table 128, taken from experiments of Billiter,[1] illustrates this behaviour; it also shows the above-mentioned reversal of the kataphoretic migration when the second sol gains the upper hand in the number of particles.

TABLE 128

Coagulation of As_2S_3 Sol by Fe_2O_3 Sol

Mg. Fe_2O_3 in 10 c.c. of Mixture.	Mg. As_2S_3 in 10 c.c. of Mixture.	Remarks.
0·61	20·3	Turbidity migrates to *anode*.
6·08	16·6	Immediate flocculation; remainder migrates to *anode*.
9·12	14·5	Almost complete flocculation.
15·2	10·4	Immediate flocculation: remainder migrates to *cathode*.
24·3	4·14	After some time fine turbidity; migrates to *cathode*.
27·4	2·07	No change, the particles migrate to *cathode*.

Ellis[2] has shown that in the flocculation of an oil emulsion by a Fe_2O_3 sol we are dealing with relationships similar to those of coagulation by electrolytes. Upon addition of the positive Fe_2O_3 sol to a negative oil emulsion the oil-drops are discharged; with the addition of still more Fe_2O_3 they become positively charged. Flocculation occurs below a certain critical potential; this amounted to $-0{\cdot}045$ volt when approached from the negative side, and to about $+0{\cdot}03$ volt when approached from the positive side. The positive particles therefore discharge the negative ones. This discharge does not result solely from the fact that the particles are oppositely charged; for they are not free charged particles, but each is enveloped in a double layer. But this double layer is diffuse, and just as this fact is responsible for kataphoresis, it must also lead to a discharge when the oppositely charged particles approach sufficiently near. The particles, to a great extent discharged, then behave just as do the particles discharged by electrolytes. As soon as the lower limit of the first critical charge is passed, flocculation occurs, because no influence exists to oppose the adhesion of the particles to one another. Since it is not necessary that the particles should completely neutralize one another, a certain degree of discharge sufficing, complete coagulation is observed not only at a definite ratio between the quantities of the two particles, but over a comparatively large range of different ratios (see Table 128). The coagulation will probably be particularly rapid when the particles neutralize one another as sharply as possible.

If this view is correct, that flocculation depends mainly upon the mutual discharge of the particles, then at the optimum of flocculation (in Table 128 at a ratio of 9·12 Fe_2O_3 to 14·5 As_2S_3) the total charge of the positive particles contained in the mixture of sols should be equal to the total charge of the negative particles. This consequence has not yet been strictly tested. It assumes that we know, besides the optimum ratio, the charge from kataphoresis measurements and the number of particles from ultramicroscopic counts. The number is difficult to deter-

[1] Zeitschr. f. physik. Chemie, **51**, 142 (1905).
[2] Zeitschr. f. physik. Chemie, **89**, 145 (1915).

mine in the case of the positive hydroxide sols, which have of necessity been used, since they are rich in amicrons.

The following experimental data favour this view. For the optimum of coagulation, the amount A^- of the disperse phase of a negative sol requires the amounts A_1^+, B_1^+, C_1^+ . . . of various positive sols ; the amount B^- of a second negative sol requires the amounts A_2^+, B_2^+, C_2^+. . . . If it is only a question of neutralization, then should

$$\frac{A_1^+}{A_2^+} = \frac{B_1^+}{B_2^+} = \frac{C_1^+}{C_2^+} \cdots$$

For if the amount B^- carried twice the charge, the amounts A_2^+, B_2^+, C_2^+ . . . . should be twice as large as A_1^+, B_1^+, C_1^+. . . . Table 129 contains measurements of such amounts A_1^+, B_1^+, C_1^+ . . . according to experiments by W. Biltz and to unpublished experiments by Pape.

TABLE 129

Ratios of the Amounts of the Micellæ of Positive Sols at the Optimum of Coagulation

Positive Sol.	Ratio of the Amounts of Micellæ of Positive Sols.			
	From Biltz's Experiments.		From Pape for complete Coagulation.	
	For 28 mg. Sb_2S_3 and 24 mg. As_2S_3 resp.	28 mg. Sb_2S_3 1·4 mg. Au resp.	10 mg. Sb_2S_3 10 mg. As_2S_3 resp.	10 mg. V_2O_5 10 mg. As_2S_3
Fe_2O_3 Sol	$\frac{32}{13} = 2{\cdot}5$	$\frac{32}{3} = 10{\cdot}7$	$\frac{7{\cdot}5}{2{\cdot}0} = 3{\cdot}8$	$\frac{33{\cdot}1}{2{\cdot}0} = 16$
Cr_2O_3 Sol	$\frac{3{\cdot}0}{0{\cdot}5} = 6$	$\frac{3{\cdot}0}{0{\cdot}3} = 10$	$\frac{1{\cdot}3}{0{\cdot}3} = 4{\cdot}3$	$\frac{9{\cdot}6}{0{\cdot}3} = 32$
Al_2O_3 Sol	$\frac{2{\cdot}0}{2{\cdot}0} = 1$	$\frac{2{\cdot}0}{0{\cdot}1 - 0{\cdot}2} = 13$		
ThO_2 Sol	$\frac{20}{6} = 3{\cdot}3$	$\frac{20}{2{\cdot}5} = 8$		
CeO_2 Sol	$\frac{11}{4} = 2{\cdot}7$	$\frac{11}{4} = 2{\cdot}7$		
ZrO_2 Sol .	$\frac{6{\cdot}5}{2} = 3{\cdot}2$	$\frac{6{\cdot}5}{1{\cdot}6} = 4$		

We may not speak of an equality of the ratios $\frac{A_1^+}{A_2^+}$ . . . ; but if we consider how greatly and rapidly, especially with fresh sols, the number of particles and the charge may change (cf. p. 456) and that this circumstance has been scarcely, if at all, taken into account, the existing parallelism may be interpreted in favour of the view above discussed. In agreement with it, further, is the fact mentioned by Galecki and Kastorskij,[1] that an amicronic gold sol required a larger amount of a Fe_2O_3 sol for the attainment of the optimum of coagulation than one more submicronic:

[1] Kolloidzeitschr. **13**, 143 (1913).

the surface of the particles was greater in the case of the amicronic sol, while the charge per unit of surface was practically the same. They also observed, moreover, the mutual coagulation of two sols directly under the ultramicroscope.

One can naturally also consider the possibility that besides mutual neutralization a specific adsorption between the particles plays an active part.[1] It would not then be necessary that the ratio of amounts corresponding to equal charges should determine the optimum of coagulation. This would be displaced to another ratio on account of the adsorptive power. The divergencies from the expected behaviour in Table 129 are perhaps to be referred to this cause.

The mutual adsorption of oppositely charged colloid particles may now be compared without further question with the adsorption of the disperse phase of lyophobic sols by adsorbents such as kaolin, fibrous Al_2O_3 (from Al amalgam) and other substances. Such experiments have shown [2] that often an adsorption in the ordinary sense does not appear to occur. The whole behaviour is again such as to suggest that it depended upon the neutralization of the opposite charges of adsorbent and disperse phase. Positive colloid particles are taken up only by negative adsorbents, thus, for example, Fe_2O_3 particles by bole, not by fibrous alumina; conversely, negative particles only by positive adsorbents, for example, As_2S_3 particles by fibrous alumina, not by bole. Only the amphoteric charcoal takes up both. But in no case, not even in that of charcoal, does an adsorption isothermal hold; the quantity taken up is, on the contrary, constant and independent of the content of the solution, as should be the case with a neutralization. A saturation is improbable when we consider how small in comparison with the high molecular weight of the micellæ is their molar concentration in the solution. As an example we may take Table 130, which contains measurements of the taking-up of As_2S_3 particles by fibrous alumina and of Fe_2O_3 particles by bole and blood charcoal.

The interaction between $BaSO_4$ and colloidal solutions discovered by Vanino[3]—Au, Ag, and As_2S_3 sols may be decolorized by shaking with it—depends upon nothing else than the "adsorption" just described; $BaSO_4$ is positive in pure water and also in feebly alkaline solution[4]; the sols concerned are negative.

Also the behaviour when particles of the one sol are in excess is entirely intelligible from this point of view. The particles present in smaller amount are neutralized by those oppositely charged. Of these, however, a large excess remains, and these excess particles when they encounter discharged particles can associate with and recharge them, on occasion to a point above the first critical charge. If the coarser flocculi produced by association remain small enough to execute a rapid Brownian motion, they remain in colloidal solution. Otherwise they settle, and we have the case of partial coagulation.

It is possible that the simple behaviour just described, that only oppo-

[1] *Bancroft*, Journ. Phys. Chem. **19**, 362 (1915).

[2] *Freundlich* and *Poser*, Kolloidchem. Beiheft. **6**, 311 *et seq.* (1914); *Carli*, Zeitschr. f. physik. Chemie, **85**, 263 (1913); further *W. Biltz* [Ber. d. deutsch. chem. Ges. **37**, 1766 (1904)], who investigated the taking-up of the micellæ of various hydrophobic sols by silk, at boiling-point however.

[3] Ber. d. deutsch. chem. Ges. **35**, 662 (1902); see further *Zsigmondy*, "Kolloidchemie," 3rd Edition, pp. 172–173 (1920).

[4] From unpublished work by *Gyemant*.

TABLE 130

"Adsorption" of the Micellæ of Hydrophobic Sols by various Adsorbents

Content of Sols after Adsorption, mg. per litre.	Amount of Micellæ (in mg.) taken up per gram of Adsorbent.
"Adsorption" of the micellæ of an As_2S_3 sol by fibrous alumina:	
1,080	16·9
2,941	16·6
6,342	17·0
"Adsorption" of the micellæ of a Fe_2O_3 sol by bole:	
162	6·65
256	6·05
486	6·6
488	7·3
949	6·95
"Adsorption" of the micellæ of a Fe_2O_3 sol by blood charcoal:	
155	9·0
284	7·5
480	8·2
1,126	6·7
1,220	7·5
1,246	8·2

sitely charged micellæ are taken up by distinctly heteropolar adsorbents such as alumina and bole, does not hold so generally as was here first assumed. It has already been emphasized above (p. 476) that particles of like charge can associate. Further, it must be remembered that the more hydrophilic are the sols with which we are dealing, the more easily can an ordinary adsorption of their micellæ by adsorbents of like charge occur. Thus W. Biltz[1] found that the particles of the negative V_2O_5 sol are taken up by amphoteric silk, and those of the likewise negative molybdenum blue sol by silk and by cotton, which is certainly negative—and also by positive Al_2O_3—according to the ordinary adsorption isothermal, just as the particles of a benzopurpurin solution are adsorbed by cotton.

In the interaction of oppositely charged sols, the manner of mixing, above all the rapidity of the same, is of the greatest importance. If the second sol is added quite gradually, the ratio corresponding to the optimum of coagulation must necessarily be passed through, and the mixture then flocculates. If we wish the second sol, when added in excess, to cover the particles of the other, it must be added quickly, so that the time during which the proportions of the mixture correspond with the optimum of coagulation is as short as possible. It is likewise necessary that the mixing shall be done very evenly, otherwise owing to local differences in content the particles will probably by no means be uniformly discharged even at the optimum of coagulation.

The mutual flocculation of oppositely charged sols is also an important and widespread phenomenon. Thus in the clarification of effluents by means of ferric salts, referred to above (cf. p. 468), coagulation by the

[1] Ber. d. deutsch. chem. Ges. **38**, 2963 (1905); further *ibid.* **37**, 1766 (1904).

colloidally charged ferric hydroxide plays a scarcely less important part than the influence of the ferric ion.[1] Also the treatment with charcoal or bole, which has recently been widely applied therapeutically, depends, at least partially, upon adsorption of bacteria by these adsorbents; upon a phenomenon, therefore, that belongs to this group of processes. It is true that the behaviour of bacteria in suspension must usually be regarded rather as hydrophilic than hydrophobic (cf. p. 607). Perhaps connected with this is the fact that when they are taken up by adsorbents, the influence of the charge apparently recedes in importance compared with a general, strong power of adsorption; charcoal is again particularly prominent in this respect, and a certain symbasis with the adsorption of methylene blue exists.[2]

Flocculation of Lyophobic Sols in the Electric Current

In the kataphoresis of hydrophobic sols we observe how the particles migrate to one pole, the negative to the anode, the positive to the cathode, and are there flocculated. They are obviously discharged at the electrodes, and the same processes take place there as in the coagulation by electrolytes. Other processes also play a part. Ions which flocculate more strongly may be formed by the electrolysis, or the concentration of ions already present may be raised to such an extent as to lead to coagulation.[3] Finally, the further possibility exists that the charge of the particles may be reversed in sign by such ions, and then mutually flocculate one another. Even slight differences of potential suffice to produce this effect. W. Biltz[4] dipped two different metals with a closed external circuit into sols, and observed a speedy flocculation of a Fe_2O_3 sol even with metals, such as zinc and iron, which are relatively near in the electrochemical series. In these experiments the micellæ generally flocculated before they reached a pole. That the kataphoresis is, however, of importance can be inferred from the fact that the particles of a positive sol are precipitated at the more noble metal, those of a negative sol at the less noble one.

Upon this coagulation by an electric current depends a curious and important phenomenon first observed by Fichter and more closely investigated by Frl. Sahlbom.[5] If sols are subjected to capillary analysis, by allowing them to rise in strips of dry filter paper, negative sols rise as high as pure water; positive sols, on the other hand, coagulate to a thick gel immediately above the point at which the paper meets the liquid, while the pure water rises higher. This does not depend upon the flocculation of oppositely charged colloids just discussed, for if the paper is first saturated with pure water and then dipped in the positive sol, its particles are not coagulated, but only one-sixth to one-eighth of the amount is adsorbed by the paper. Negative sols also do not rise high in the wetted paper, since this rise depends upon the colloid particles being carried up with the liquid. The penetration of the liquid into the dry paper is therefore important both for the rise of the negative sol and the coagulation of the positive one. Other structures with fine pores behave like paper;

[1] See *W. Biltz* and *Kröhnke*, Zeitschr. f. angew. Chemie, **28**, 883 (1907).

[2] See *Bechold*, Kolloidzeitschr. **23**, 35 (1918). He investigated staphylococci and bacterium coli.

[3] See e.g. *Schmauss*, Ann. d. Physik (4), **18**, 628 (1905).

[4] Zeitschr. f. Elektrochemie, **14**, 567 (1908).

[5] Kolloidchem. Beiheft. **2**, 79 (1910).

for example, tubes filled with quartz sand, shellac, or sulphur granules, and even simple glass capillaries with a diameter of less than 0·15 mm. show the effect. If a dry capillary is dipped into a positive sol—e.g. a Fe_2O_3 sol—flocculi are immediately formed in the point, while negative sols simply rise in the capillary. It may be remarked that the capillaries of the paper are naturally fine enough to allow the phenomena to be regarded as of the same kind; they had on the average a diameter of about 0·05 mm.

Frl. Sahlbom explains the phenomenon correctly in the following manner. As the sol penetrates into the dry paper a stream-current is formed. Its potential drives the colloid particles by kataphoresis against the wall of the capillary, where they are coagulated in the manner just considered, provided that they are oppositely charged. Since the wall-layers of the substances in question, such as paper, quartz, etc., are negatively charged, the particles of positive sols are coagulated. The particles of negative sols cannot be discharged and flocculated under these experimental conditions. In agreement with this view is the fact that acids favour the rise of positive sols. In the first place they peptize, and thus make the particles smaller and charge them more strongly; then they diminish the charge on the wall, and may sometimes even reverse it; all circumstances which oppose the flocculation as the liquid penetrates the paper.

This capillary analysis forms a useful method for deciding quickly whether a sol is positive or negative, provided that the amount of disperse phase is not so small that mere adsorption by the paper can mask the rise in the case of a negative sol.

That a certain caution is necessary in applying this method is rightly emphasized by Thomas and Garrard.[1] They found, on the one hand, that very dilute Fe_2O_3 and Cr_2O_3 sols can rise in filter paper, whilst very concentrated As_2S_3 sols are coagulated. This was confirmed; a dilute Fe_2O_3 sol, proved positive by kataphoresis, showed a noticeable rise, a concentrated negative V_2O_5 sol was strongly coagulated immediately above the point of immersion. Such behaviour is to be expected; for if a positive sol is very dilute, the time required for the micellæ to reach the walls of the fibres may be considerably greater than in the case of a concentrated sol, since the pores are clogged much more slowly. In comparison with this the rise may be fast enough to drag micellæ upwards. With a very concentrated negative sol coagulation by impurities of a saline nature in the paper may become important; with an old, concentrated V_2O_5 sol we may also suppose that the rod-shaped particles may very easily clog the pores of the paper.

Flocculation by other Influences

It has been frequently observed that hydrophobic sols are flocculated when shaken with non-miscible liquids, such as benzine, benzene, carbon disulphide, and so on.[2] The particles collect at the boundary between the two liquids, the gold particles, for example, as a beautiful glistening golden skin. In contradiction with this is Zsigmondy's [3] statement, that

[1] Journ. Amer. Chem. Soc. **40**, 101 (1918).

[2] *Winkelblech*, Zeitschr. f. angew. Chemie, **19**, 1953 (1906); see also *Jordis*, Zeitschr. f. Elektrochemie, **13**, 540 (1907); *Lash Miller* and *McPherson*, Journ. Phys. Chem. **12**, 706 (1908); *Corliss*, *ibid.*, **18**, 681 (1914).

[3] Zeitschr. f. Elektrochemie, **22**, 102 (1916); Zeitschr. f. anorg. allgem. Chemie, **96**, 265 (1916).

colloidal gold solutions are not coagulated when such experiments are carried out under the cleanest possible conditions. Zsigmondy was able to explain this contradiction. As long as the colloid particles were small enough, they were not flocculated; this occurred, however, immediately they became larger, irrespective of whether they were larger from the outset, or were formed from smaller particles by coagulation. Since gold sols are extremely sensitive to foreign impurities, even very small amounts suffice to coarsen the particles to such an extent that they are coagulated; thus contamination introduced from the finger used to close the test-tube for shaking is sufficient to produce flocculation (see p. 586).

That coarser particles, on shaking with non-miscible liquids, collect at the interface is intelligible from the considerations on p. 159. The particles of the metals and sulphides, and to a lesser degree those of the oxides and hydroxides, are throughout hydrophobic. The organic liquid must displace the water from the surface, as described in the place referred to above, and the particles therefore collect at the interface.

It is more difficult to explain why the small particles do not show this effect. One might at first suppose that this depends on the greater charge of small particles. Upon shaking the liquids, drops of the organic liquid, which are always negative, are emulsified in the sol. Since they have a charge similar to that of the colloid particles, the tendency to associate will be particularly slight when the particles of the gold sol are themselves very decidedly negatively charged. But this explanation can be only in part correct. For if a gold sol prepared by electrical disintegration, which contains many coarse particles together with the finer ones, is shaken with benzene, the coarser particles are shaken out, the finer ones remain in colloidal solution. Here we cannot suppose that the coarser particles have a smaller charge.

We must rather assume with Zsigmondy, that with the very small particles, the interfacial forces and therefore the attraction between the particles and the organic liquid are altered. If the gold particle, for example, is very small, then the H_2O molecules which take part in the structure of the micella will now be of importance for its interfacial tension. The interfacial tension between micella and water, σ_{sA} (see p. 159) is smaller than in the case of a larger micella. The conditions which must be fulfilled for transition to the organic liquid or for collection at the interface respectively,

$$\sigma_{sA} \geqq \sigma_{sB} + \sigma_{AB},$$

will no longer hold; for σ_{AB} has the old value, and σ_{sB}, the interfacial tension between micella and organic liquid, will hardly be so greatly changed by the influence of the H_2O molecules. With very small particles therefore the conditions for a displacement of the water by the organic liquid, the preliminary condition for collection at the interface, become increasingly less favourable. Hence it is a question fundamentally of the water envelope, which is particularly effective in the case of small particles. The alteration in the interfacial forces, which is here assumed, might also be connected with the fact that the interfacial tension of the particles against the surrounding liquid necessarily decreases with decrease in size of particle (cf. p. 46).

The inability of small particles of a gold sol to amalgamate by shaking with mercury is similarly due to this cause.

Discharges from electrodes external to the liquid, *point discharges*, etc., do not, according to Spring's[1] experiments, affect the stability of lyophobic sols. This is intelligible when we consider how small are the amounts of electricity which are hereby set in motion, and how great are the amounts necessary for flocculation.

According to Spring, *X-rays* also have no effect. On the other hand, Galecki[2] observed that a gold sol prepared by Zsigmondy's formaldehyde method was coagulated by them, but apparently only the coarser particles were affected. The number of submicrons visible in the ultramicroscope decreased during exposure to the rays, but the red colour of the sol was only slightly altered, doubtless because the much larger number of fine particles remained unchanged.

That the *rays of radio-active substances* can flocculate hydrophobic sols may be taken as certain. The first trustworthy statement in this direction is due to V. Henri and A. Mayer.[3] According to them the β-rays of radium discharge and coagulate positive sols, such as ferric hydroxide, etc., but not negative sols. Jorissen and Woudstra[4] confirmed these observations. The effect with Fe_2O_3 sols was, however, well marked only when the charge of the particles had been depressed by addition of electrolyte. Particularly beautiful and striking is the action of the rays upon positive ceric hydroxide sols, which was discovered by Fernau and Pauli.[5] This sol behaves upon coagulation like an Al_2O_3 sol. It becomes more and more viscous and finally a stiff jelly. While the sol, left to itself, showed no tendency to coagulate for over a year, it set in 24 hours to a stiff jelly when exposed at 18° to the radiation from 22 mg. of radium barium carbonate. The radio-active material was contained in a glass tube; this dipped into the sol, and 20 per cent. of the β radiation, and 99 per cent. of the γ radiation, penetrated 2·5 centimetres of the sol.

When the time course of the coagulation was followed from the alteration in viscosity, a distinct decrease first occurred. This was followed fairly suddenly by a strong rise. The investigators named above correctly explained this behaviour as follows. The decrease in viscosity depends upon the discharge of the particles, as is to be expected in accordance with Smoluchowski's theory discussed above (p. 439). It therefore corresponds to the decrease frequently observed upon ageing. The strong rise is due to the association of the hydrophilic flocculi which are to a great extent discharged (see p. 440). Only the discharge and the decrease in viscosity appear to be caused by the radium radiation, for the rise in viscosity also occurs when the radium preparation is removed from the sol at the moment when the viscosity is at a minimum. In the coagulation of a CeO_2 sol by NaCl a decrease and increase in viscosity is likewise observed; but the decrease occurs rapidly, immediately after the addition of electrolyte, and the increase then sets in at once, without, however, reaching such a high value. The difference probably depends upon the fact that the discharge is more gradual in the case of radium radiation than by addition of electrolyte; discharge of the particles and association of the partially discharged particles to coarser flocculi are intermingled and produce the altered effect. The further observation is curious, that

[1] Bull. Acad. Roy. Belg. **1900,** 483; Rec. d. trav. chim. d. Pays-Bas, **19,** 204 (1900).
[2] Kolloidzeitschr. **10,** 149 (1912).
[3] Compt. rend. **138,** 521 (1904).
[4] Kolloidzeitschr. **8,** 8 (1911); **10,** 280 (1912).
[5] Biochem. Zeitschr. **70,** 426 (1915); Kolloidzeitschr, **20,** 20 (1917).

with gentle coagulation by radium rays, that is, when the radium preparation is removed before the rise in viscosity occurs, the latter, after attaining a maximum, decreases again; the sol re-peptizes. Fernau and Pauli explain this on the grounds that charged particles are initially enclosed in the flocculi during the formation of the gel. If the discharging influence ceases to act, the charge distributes itself again more evenly and causes a fresh charging of the flocculi and peptization. The H_2O_2 resulting from the irradiation of the water plays no direct part in the phenomenon, for addition of it has no influence upon the stability of CeO_2 sols.

A considerable amount of data exists concerning the flocculating action of light. Two kinds of processes must here be distinguished; a simple coagulation, in which the particles associate under the influence of light, and settle on account of gravity, and a *photophoresis*, in which they move under the influence of light in a certain direction; a *positive* photophoresis when they move towards the light, and a *negative* one when they move away from it. If this photophoresis should occur without coagulation, it would, even by itself, injuriously affect the stability of sols.

In a case investigated by Nathansohn [1] it appeared that the action of light is only indirectly the cause of coagulation. A diluted amicronic As_2S_3 sol becomes turbid on illumination with a nitra lamp, and the F.V. for electrolytes is distinctly reduced (by about 50 per cent.). But this action depends upon the fact that light causes a permanent change even in an electrolyte-free As_2S_3 sol. An illuminated, not yet turbid As_2S_3 sol shows the same depression of the F.V. on coagulation by electrolytes in the dark, as when the flocculation by electrolytes is produced directly in the light. By illumination, a very highly disperse sulphur sol is formed, probably by an oxidation of the H_2S formed by hydrolysis of As_2S_3, an oxidation which is accelerated on the As_2S_3 particles by the action of light. The presence of sulphur micellæ in the illuminated As_2S_3 sol may be recognized as follows. During kataphoresis, whitish sulphur micellæ separate from the yellow As_2S_3 micellæ, and upon illumination of an electrolyte-free As_2S_3 sol a white sediment of sulphur is formed in course of time.[2] It was stated above (p. 477) that a mixture of an As_2S_3 sol and an Odén sulphur sol becomes turbid and shows lower flocculation values than the pure sols. The colloidal sulphur produced by light may act in the same way upon an As_2S_3 sol. Externally the coagulation by electrolytes in the presence of light is distinctly different from ordinary coagulation. In light, solitary flocculi, which slowly settle, arise in the interior of otherwise clear sols, while in coagulation not influenced by light the sol becomes uniformly turbid and a copious flocculation appears in the whole liquid.

Stintzing [3] described an example in which coagulation and photophoresis are combined. A solution of silver resinate in oil of lavender or benzene is colloidal. When viewed under the ultramicroscope flocculation appeared under the influence of light, the particles originally in lively molecular motion united to coarser, immobile flocculi. In order to make the positive photophoresis more plain, the solution was illuminated through

[1] *Freundlich* and *Nathansohn, loc. cit.* p. 476.

[2] *W. S. Young* and *Pingree* [Journ. Phys. Chem. **17**, 657 (1913)], using, however, considerably stronger illumination, believe that they have observed, with As_2S_3 and other sols, a direct decrease in the kataphoretic migration velocity, which *Nathansohn* did not find with As_2S_3 sols.

[3] Kolloidchem. Beiheft. **6**, 231 (1914); further *Schaum*, Zeitschr. f. Wiss. Photograph. **12**, 93 (1913).

a quartz cover, the inner side of which touched the solution, while the outer side was covered with black paper in which letters had been cut. The silver was deposited preferentially at the illuminated points. Ultraviolet light was particularly effective. Since the phenomenon of photophoresis will be discussed more in detail later, the reader is referred thereto (p. 786).

The Chemical Behaviour of the Disperse Phase of Lyophobic Sols

The chemical behaviour of the particles of lyophobic sols may be distinguished by the fact that the disperse phase often appears reactive as compared with the same substance in mass; on the other hand, when we think of similar substances in true solution, it appears at times to be rather sluggish; we are dealing with substances which are finely divided, but still usually solid.

The following examples of rapid reactions may be mentioned.

An As_2S_3 sol is almost instantaneously decolorized by alkali.

J. M. Jaeger and de Boer [1] describe the following remarkable process. A green negative ruthenium sulphide sol, the particles of which have the composition RuS_6, passes by oxidation into a red positive sol; with HNO_3 the reaction is violent.

In ordinary Fe_2O_3 sols prepared in the cold, H_2S immediately throws down black sulphide.[2]

Some silver chloride is always produced during the flocculation of Ag sols by chlorides. In Carey Lea sols this process is associated with a simultaneous reduction of the ferric citrate which is present in small amount. The more ferric ion is reduced to ferrous, the more silver is chlorinated.[3]

If to Ag sols (F. Wöhler or Carey Lea) a quantity of chlorine water insufficient to chlorinate fully be added, a sol of the photochloride, that is, a mixture of silver and silver chloride, is formed [4] (see p. 803).

MnO_2 sols dissolve in H_2O_2 solution (in the absence of alkali) to a colourless solution, without a catalytic decomposition of the H_2O_2 taking place. The solution contains a manganous salt of H_2O_2 acting as an acid; that is, a compound $Mn\langle{}^{O}_{O}\!\!>\!\!\!|\!\!|$, a labile isomer of pyrolusite $Mn\langle{}^{O}_{O}\!\!>$.[5]

The last case shows how a substance may be successfully employed in colloidal solution in order to bring it into effective reaction. In a certain sense as much or more is attained as when the substance is employed in the form of an extremely fine powder.

The following examples produce the impression of a certain sluggishness of reaction.

Although the Fe_2O_3 in Fe_2O_3 sols dissolves in acids, the flocculation value with acids can still be determined, even with acids such as HCl or HNO_3 with univalent anions, which only flocculate in considerable concentrations, for the flocculation proceeds much more quickly than the chemical reaction.[6]

[1] Koninkl. Akad. v. Wetensch. Amsterdam, **29**, 29 (1920).
[2] *E. A. Schneider*, Ber. d. deutsch. chem. Ges. **24**, 2242 (1891).
[3] *E. A. Schneider*, Ber. d. deutsch. chem. Ges. **25**, 1440 (1892).
[4] *Baur*, Zeitschr. f. physik. Chemie, **45**, 613 (1903).
[5] *Bredig* and *A. Marck, van Bemmelen*-Festschrift, p. 342 (1910).
[6] *Freundlich*, Zeitschr. f. physik. Chemie, **44**, 150 (1903).

The silver in silver sols (Bredig's) dissolves slowly in HNO_3 and H_2SO_4; curiously enough rapidly upon addition of a few drops of a permanganate solution.[1] This indicates that some kind of difficultly soluble surface layer envelopes the particles and opposes solution.

We may regard the fact that many sols are quite tasteless as a sign of sluggish reactivity.[2]

Reactions are known in which two sols act upon one another with the formation of a sol with chemically different micellæ.[3] If a grey-green silver sol (Carey Lea) be mixed with a sulphur sol (Weimarn or Odén) the initially brown liquid passes through a series of colours—wine red, violet, steel blue, greenish—into a pale yellow-brown sol. This is a Ag_2S sol. Ultramicroscopically a characteristic change in the appearance of the micellæ can be recognized. Whether it is a question of a direct interaction of the micellæ, or whether it depends upon other substances present in the sol (H_2S, $Ag^{\cdot}$ ions, and the like) is still an open question. The manifold colours probably depend upon the production of micellæ containing both Ag and Ag_2S. Similar colours are known in the case of the photochlorides to be discussed later (p. 803), which are mixtures of silver and silver halide. Corresponding processes, in part also with peculiar colour changes, have been observed [4] in the interaction of a Carey Lea silver sol with an As_2S_3 sol and of a sulphur sol (Odén) with selenium sols (according to H. Schulze [5] and Kruyt). If we are really dealing with direct reactions between the micellæ, it is worthy of note that all these sols were equally negatively charged.

Chemical changes have frequently [6] been described which are experienced by colloidal solutions in light, particularly in the strong illumination of the cardioid ultramicroscope. In silver halide sols variously coloured micellæ of the metal appear; sols of dyes such as benzopurpurin, dimethylaminoazobenzene and others become molecularly disperse, and so on. An explanation of these processes has not yet been successful in any case.

Acceleration and Inhibition of Chemical Reactions by Lyophobic Sols

Cases have hardly yet been examined in which colloid particles participate in an actual chemical equilibrium. Such equilibria will occur frequently enough in the micellæ, closely connected with adsorption equilibria. But the chemical properties of a micella still await explanation from the quantitative side (p. 371). On the other hand, the catalytic actions of hydrophobic sols have been investigated in detail on account of their curious nature. This is particularly true in the case of positive catalysis by metallic sols.

[1] *McIntosh*, Journ. Phys. Chem. **6**, 17 (1902).

[2] E.g. Sb_2S_3 sols, according to *H. Schulze* [Journ. f. prakt. Chemie, **27**, 326 (1883)]; Au sols according to *Zsigmondy* [Lieb. Ann. **301**, 34 (1899)].

[3] *Freundlich* and *Nathansohn*, Kolloidzeitschr. **29**, 16 (1921).

[4] *Kruyt* and *A. E. van Arkel*, Rec. d. trav. chim. d. Pays-Bas, **39**, 656 (1920).

[5] Journ. f. prakt. Chem. **32**, 390 (1885).

[6] See particularly *Siedentopf*, Verh. d. deutsch. phys. Ges. **12**, 33 (1910); Kolloidzeitschr. **6**, 3 (1910); Ber. d. deutsch. chem. Ges. **43**, 692 (1910); *W. Biltz*, Kolloidzeitschr. **12**, 296 (1913); further also *Kruyt* and *Kolthoff*, Kolloidzeitschr. **21**, 26 (1917).

Positive Catalysis by Hydrophobic Sols

Best known, through the work of Bredig and his pupils,[1] are the catalytic actions of metallic sols, particularly of platinum hydro-sols. These accelerate the same reactions as are also accelerated by platinum black—the decomposition of hydrogen peroxide and of hypochlorous acid, the oxidation of chromous salts, that of iodides by atmospheric oxygen and of NH_3 by permanganate, the combination of oxyhydrogen mixture, and many others. Both *macroheterogeneous catalysis* by platinum foil and *microheterogeneous catalysis* by platinum sols have been investigated in a series of cases; and a comparison is frequently so instructive, that macroheterogeneous catalysis will be discussed here, although it naturally belongs to the section dealing with adsorption catalysis (see p. 225).

These cases include the decomposition of hydrogen peroxide according to the equation

$$2H_2O_2 = 2H_2O + O_2.$$

The macroheterogeneous catalysis on platinum foil coated with platinum black has been investigated by Bredig and Teletow.[2] Their experiments may be interpreted throughout upon the assumption that the time-course is determined by the diffusion of the H_2O_2 to the surface of the platinum, and that the decomposition takes place much more quickly upon the surface. There it probably depends less upon an adsorption catalysis than upon a chemical interaction with the platinum, perhaps upon the formation of an unstable oxide and its decomposition.[3] The principles of the theory of Nernst and Brunner (see p. 146) will therefore apply. Decomposition takes place in neutral, acid, and alkaline solution according to a reaction of the first order. The velocity constant is proportional to the $\frac{2}{3}$ power of the rate of stirring and the first power of the area of the surface of the platinum black, and inversely proportional to the volume of the liquid. Substances which retard diffusion also retard the velocity of decomposition; in a solution containing 5 per cent. of cane-sugar the constant was 33 per cent. smaller. The thickness of the boundary layer, through which diffusion took place, was about 16 to 50 μ.

Now, microheterogeneous catalysis with platinum sols differed in a very decided manner. It is true that the decomposition proceeded in neutral and feebly acid solution [$(NH_4)_2HPO_4$] according to a reaction of the

[1] *Bredig* and *Müller v. Berneck*, Zeitschr. f. physik. Chemie, **31**, 258 (1899); *Bredig* and *Ikeda*, *ibid.* **37**, 1 (1901); *Bredig* and *Reinders*, *ibid.* **37**, 323 (1901); *Bredig* and *Fortner*, Ber. d. deutsch. chem. Ges. **37**, 798 (1904); *Spear*, Journ. Amer. Chem. Soc. **30**, 195 (1908); *Brossa*, Zeitschr. f. physik. Chemie, **66**, 162 (1909); *McBain*, "Die Zersetzung des Chromochlorürs an Kolloidem Platin," Diss., Heidelberg, 1909; *Bredig* and *A. Marck*, *van Bemmelen*-Festschrift, p. 342; Denham, "Zur Kenntnis der Katalyse in heterogenen Systemen; Die Zersetzung der Titansalze durch Platin," Diss., Heidelberg, 1909.

[2] Zeitschr. f. Elektrochemie, **12**, 581 (1906); also *Teletow*, "Katalytische Reaktionsgeschwindigkeit in heterogenen Systemen: Vergleich der Zersetzung des Wasserstoffsuperoxyds an Platinblechen mit der Kolloidkatalyse," Diss., Heidelberg, 1906.

[3] *Haber*, Zeitschr. f. anorg. Chemie, **18**, 40 (1898); Zeitschr. f. physik. Chemie, **34**, 513 (1900); Zeitschr. Elektrochemie, **7**, 441 (1901). The possibility must be taken into account that the chemical action of an oxide of platinum is to be distinguished from that of the metal, as *Willstätter* has observed in hydrogenations by means of platinum. [*Willstätter* and *Hott*, Ber. d. deutsch. chem. Ges. **45**, 1471 (1912); *Willstätter* and *V. L. King*, *ibid.* **46**, 527 (1913); *Willstätter* and *Jaquet*, *ibid.* **51**, 767 (1918)].

first order, as Bredig and Müller von Berneck found, and as Table 131 shows.

TABLE 131

Velocity of Decomposition of H_2O_2 by a Platinum Sol

Pt content = 6·2 mg. per litre; t = 25°.

t (in minutes).	c of the H_2O_2 Solution (mol per l.).	$k = \frac{1}{t} \log \frac{c_0}{c}$.
0	0·0227	—
10	0·01375	0·051
20	0·00837	0·051
30	0·00493	0·051
35	0·00319	0·048

Hence one might at first think of simply transferring the diffusion theory to microheterogeneous catalysis.[1] If one then calculates the thickness δ of the diffusion layer from the constant k (cf. p. 335), for which according to the theory of Nernst and Brunner the equation

$$k = \frac{\omega D}{\delta v}$$

holds (ω being the surface area, v the volume of the liquid, D the diffusion constant), we arrive at unusually high values (about 70μ), which greatly exceed the distance apart of the particles.

It is, however, really obvious *a priori* that the simple transference of the diffusion theory will not do. The platinum particles are in continuous lively molecular motion. It is hence impossible that a diffusion layer of sensible thickness is formed. It could, at most, have the thickness of that layer of liquid which is associated with the Pt particles. Hence the following view, developed by MacInnes [2] and by Denham,[3] is perhaps more probable. Microheterogeneous catalysis with platinum sols depends especially upon adsorption; the H_2O_2 is very rapidly adsorbed upon the surface of the micellæ, and we measure the smaller velocity of a chemical decomposition of the H_2O_2 at the interface. It may therefore remain an open question for the present whether the decomposition is simply an adsorption catalysis, or whether the adsorbed H_2O_2 reacts with the Pt (or with a compound of the same).

Some facts appear to be in good agreement with this view. Thus an equation for a reaction of the first order holds only approximately; especially with active Pt sols of high content, the constant rises as the peroxide concentration falls, as Table 132, which is taken from experiments by Bredig and Ikeda, shows. This behaviour would, as MacInnes first

[1] *H. J. S. Sand*, Zeitschr. f. physik. Chem. **51**, 641 (1905).
[2] Journ. Amer. Chem. Soc. **36**, 878 (1914).
[3] *loc. cit.* p. 489.

TABLE 132

Velocity of Decomposition of H_2O_2 by a Pt Sol, calculated with Adsorption taken into Account

Pt content = 2·0 mg. per litre; t = 25°.

t (in minutes).	c of the H_2O_2 Solution (mol per l.)	$k = \frac{1}{t}\log\frac{c_0}{c}$.	$k' = \frac{1}{t\left(1-\frac{1}{n}\right)}\left\{c_0^{1-\frac{1}{n}} - c^{1-\frac{1}{n}}\right\}$
0	0·0972		
6·03	0·0685	0·058	0·027
11·42	0·0475	0·063	0·028
15·85	0·0337	0·067	0·028
21·18	0·0219	0·0705	0·028
26·70	0·0139	0·073	0·027
32·10	0·0079	0·076	0·027

showed, follow at once if the velocity were proportional to the amount of H_2O_2 adsorbed. We should have

$$-\frac{dc}{dt} = k'c^{\frac{1}{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Integration gives

$$k' = \frac{1}{t\left(1-\frac{1}{n}\right)}\left\{c_0^{1-\frac{1}{n}} - c^{1-\frac{1}{n}}\right\}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the same equation, therefore, as holds for the decomposition of SbH_3 (cf. p. 141). The values of k' given in Table 132 show a satisfactory constancy.

It should be noticed that equation (1) is not a definite proof that we are dealing with a chemical reaction in the adsorption layer. It might also be arrived at in other ways. If, for example, the dissolved substance is adsorbed at the surface but then diffuses into the interior of the micellæ and thus reacts, and if this diffusion is the slowest process, we arrive at the same formula. For, according to Nernst and Brunner (see p. 335)

$$-\frac{dc}{dt} = \frac{k\mathrm{D}}{\delta v}(c_1 - c_2).$$

The determining external concentration c_1 corresponds here to that of the amount $a = ac^{\frac{1}{n}}$ adsorbed at the surface, and the concentration in the interior c_2 is zero. We therefore obtain

$$-\frac{dc}{dt} = \frac{k\mathrm{D}a}{\delta v}c^{\frac{1}{n}} = k'c^{\frac{1}{n}},$$

an equation which does not differ from (1). With the rigid particles, poor in water, of a platinum sol one will regard a diffusion of this kind into deeper layers as improbable, but not so, when the micellæ are viscous liquids and rich in water (see e.g. p. 762).

The difference between macroheterogeneous and microheterogeneous catalysis in alkaline solution is striking. It may be referred to the pecu-

liarities of colloidal solutions. With macroheterogeneous catalysis there is, as already mentioned, no essential difference between the process in alkaline and in neutral or acid solution; it takes place according to a reaction of the first order, and so on. With a platinum sol, on the other hand, the reaction is very much accelerated in dilute alkaline solution; there further exists a maximum of the effect at small concentrations of the alkali (about 30 millimols per litre); at larger concentrations the process proceeds still more slowly than in neutral solution. In Table 133 are given the times required for 50 per cent. decomposition, together with the NaOH concentrations. Fig. 114 shows the same relation graphically.

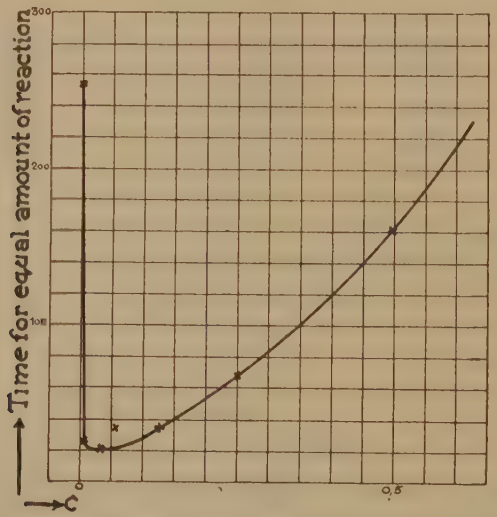

Fig. 114.—Influence of OH′ Ion upon the Catalysis of H_2O_2 by a Pt Sol.

Table 133

Influence of the OH′ Ion upon the Decomposition of H_2O_2 by a Pt Sol

Pt. content = 0·64 mg. per litre; t = 25°

[NaOH Concentration (mol per litre).	t (in minutes, for 50 per cent. decomposition).
$\frac{1}{\infty}$	255
0·00195	34
0·0039	28
0·0078	24
0·0156	25
0·03125	22
0·0625	34
0·1250	34
0·2500	70
0·5000	162
1·0000	520

It further appeared that an equation for a reaction of the first order did not hold. With small NaOH concentrations the velocity was practically independent of the H_2O_2 concentration (the reaction was therefore of zero order; see Table 134); with larger concentrations it lay between the zero and first order. The course was however somewhat irregular.

TABLE 134

Velocity of Pt Catalysis in Alkaline Solutions

Pt. content = 0·64 mg. per litre; NaOH concentration = 0·0156 mol per litre; t = 25°

t (in minutes).	*c* of the H_2O_2 Solution (mol per l.).	$k = -\frac{dc}{dt}$.
0	0·02381	—
6	0·02108	0·47
15	0·01684	0·47
25	0·01185	0·48
40	0·00568	0·47

The fact that these peculiarities do not appear in macroheterogeneous catalysis is sufficient proof that it is not the salt-like combination of H_2O_2 with alkali which is responsible for them, but rather that the Pt sol itself is influenced. The hydroxyl ion has, of course, a decided charging and peptizing action. It is able to split up submicrons into amicrons (see p. 472), and the dependence of the stability of suspensions and sols upon the OH′ ion concentration shows a maximum in just the same range of concentration (see p. 474) as here produces maximum acceleration with a Pt sol. We may therefore refer the acceleration of the decomposition in dilute alkalis at any rate in part to the increase in the surface. At higher concentrations the flocculating action of the alkali makes itself felt and again diminishes the rate of decomposition.

The time-course of the reaction may also be readily explained. At small NaOH concentrations, the amount bound by the excess of H_2O_2 (this was 0·3 to 0·5 molar) is appreciable; Calvert [1] found that in a solution which was $\frac{1}{80}$ N with regard to NaOH, $\frac{1}{40}$ molar with regard to H_2O_2, the content of free NaOH was depressed from 100 per cent. to 25 per cent. Corresponding with a disappearance of H_2O_2 by decomposition, NaOH becomes free; if therefore the OH′ ion concentration was originally depressed by the H_2O_2 below that causing maximum reaction velocity, it now approaches this value during decomposition and accelerates the latter. If this acceleration is just as great as the diminution in the amount decomposed due to the decrease in concentration of the H_2O_2, the rate of decomposition will obviously be independent of the concentration. That this can only be a fortunate coincidence is clear.

The dependence of the velocity upon the content of disperse phase has not yet been correctly explained. According to the adsorption theory we should expect the velocity to be proportional to the platinum content. The amount of Pt is so small, that the original concentration of the H_2O_2 is but little altered by adsorption. Hence we may put the amounts

[1] Zeitschr. f. physik. Chem. **38**, 527 (1901).

adsorbed proportional to the Pt content, and the velocity should be proportional to this amount of H_2O_2. McInnes[1] calculated according to equation (2) two series of experiments of Bredig and Ikeda, in which the same Pt sol was present in various dilutions, and found that, as was to be expected, the ratio of the velocity constants agreed well with that of the Pt concentrations. He obtained for the constants

$$\frac{3{\cdot}40}{2{\cdot}23} = 1{\cdot}52.$$

For the Pt concentrations

$$\frac{2{\cdot}7}{1{\cdot}6} = 1{\cdot}66.$$

As against this, Bredig and Müller von Berneck found, when they compared Pt sols of various concentrations obtained by diluting an original sol, that the velocities increased in greater degree than in simple proportion to the Pt concentrations. They were able to express the dependence by an equation

$$k = \mathrm{k}(\mathrm{Pt})^q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where (Pt) is the platinum content, k and q are constants, q having a value of 1·6. Table 135 shows how far this relation holds. The constant k was calculated from an equation of the first order, not according to equation (2).

TABLE 135

Dependence of Pt Catalysis of H_2O_2 on Pt Content

$\mathrm{k} = 0{\cdot}001058$; $q = 1{\cdot}59$; $\mathrm{t} = 25°$

(Pt) (mg. per l.).	k (obs.).	k (calc.).
5·07	0·014	0·014
10·3	0·044	0·043
20·5	0·127	0·129

It should be tested whether this is the cause of the departure from simple proportionality. If not, we must take into account the possibility, that the velocity of adsorption cannot be neglected as infinitely rapid in comparison with that of chemical reaction. We should then have in the first place an increase proportional to the Pt content on account of the increased amount adsorbed, and in addition a still more rapid increase since the lively mixing in consequence of the molecular motion causes a quicker attainment of adsorption equilibrium in the solution richer in platinum.

The flocculating action of electrolytes does not take great effect in microheterogeneous catalysis. This is due to the fact that one must work with very dilute sols, since otherwise the decomposition of H_2O_2 takes place too quickly to be measured. The highest content which can be employed with sols of normal activity is about 10 to 20 mg. per litre. Now the rapid flocculation of sols proceeds according to a reaction of the second

[1] *loc. cit.* p. 490.

order (see p. 433). This also holds, within certain limits, for slow flocculation. Hence it follows that the time required for a certain interchange is inversely proportional to the initial content (see formula (7), p. 434). In order to be able to follow conveniently the coagulation of Pt sols by electrolytes, one must use a sol at least twenty times more concentrated, of about 200 mg. per litre. With this the F.V. is determined by finding the electrolyte content which flocculates completely in 2 hours. The more dilute sols such as are employed for catalysis would therefore only be completely flocculated in about 40 hours. But since the time-course of the catalysis is usually followed over 1 to 2 hours, the coagulation occurring in this time produces very little effect. Bredig and Müller von Berneck have, it is true, observed that alkali salts and acids depress the rate of decomposition of H_2O_2 on platinum, but it is difficult to decide whether this is to be ascribed to flocculation by electrolytes; for since sulphates, for example, sometimes also have an accelerating action, one must consider the possibility of other electrolyte influences also coming into question (cf. p. 499).

The behaviour of a large number of substances which strongly inhibit the catalysis of H_2O_2 has been closely investigated. In this case we have again to decide between two effects, such as was recognized above (p. 231) in connexion with the inhibition of the oxidation of amino acids on charcoal by foreign substances. In the first place let us take the action of the distinctly capillary active organic substances, such as alcohols, ketones, urethanes, investigated by Meyerhof.[1] The action is reversible; by washing out the inhibitory substance may be removed; the dependence upon the concentration resembles an adsorption isothermal; Traube's rule holds, the action rising strongly in the homologous series. This was especially clear with the alcohols, as Table 136, calculated from Meyerhof's data, shows. The difference between the velocity constants of the cata-

TABLE 136

Traube's Rule in the Inhibition of Catalysis of H_2O_2 by Pt Sol

$t = 25°$

Substance.	Concentration c (molar) producing Inhibition of 55 per cent.	$p = \frac{c_n}{c_{n+1}}$
Ethyl alcohol	1·5	—
Propyl alcohol	0·63	2·4
i-butyl alcohol	0·40	1·6
Amyl alcohol	0·23	1·7

lysis taking place in a solution in the absence of and that in the presence of an organic substance is designated inhibition. In the case of these substances, as in the case of the oxidation of cystine on charcoal mentioned above on p. 232, it will depend upon the displacement of H_2O_2 from the interface in consequence of their adsorption. Probably we shall also find here an equal inhibitory action when the substances occupy equally large surfaces at the boundary.

There is then a second group of substances, which in part are not at all sensibly surface active, but nevertheless markedly inhibit the reaction

[1] Pflüg. Archiv, **157**, 307 (1914).

even in concentrations far lower than those of the group first named. Hydrocyanic acid was such a substance in the case of the oxidation of cystine on charcoal, and its striking influence could there be explained by its rendering inactive the particular points of oxidation on the charcoal occupied by iron compounds, by forming, after a probable preliminary adsorption, loose complex compounds with the iron (cf. p. 232). Here also, in the case of Pt catalysis, hydrocyanic acid belongs to this group of active substances, the real *poisons*. It includes further :—corrosive sublimate, iodine, cyanogen iodide, sulphuretted hydrogen, carbon monoxide, and others. The taking-up of these foreign substances likewise proceeds here in the manner of an adsorption. In the first place the degree of poisoning depends upon the concentration of the poison in a manner corresponding to the adsorption isothermal. As a measure of the poisoning Bredig and Ikeda, who closely investigated the phenomenon, employed the relative increase in the time in which half the H_2O_2 was decomposed. If therefore t_c is this time for the poisoned solution, t_0 for the unpoisoned, then

$$g = \frac{t_c - t_0}{t_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

is the degree of poisoning. The dependence of g upon the concentration c of the poison may be expressed by an equation

$$g = \alpha c^{\beta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in which α and β are constants. α has very different values for different poisons. β varies between 0·5 and 1·2. Equation (5) is obviously an adsorption isothermal. That β is sometimes greater than the usual value of the adsorption exponent $\frac{1}{n}$, should be explicable on the grounds that c in this equation is the total concentration, not the equilibrium concentration, as required by the adsorption isothermal. The abscissæ in the logarithmic graph (see Fig. 33, B, p. 173) were therefore too great; the divergences from the equilibrium concentration being the greater, the smaller the concentration; but if the same ordinates with decreasing concentration are plotted against abscissæ increasingly too large, the log a, log c curve will be too steep and the adsorption exponent too large. How far formula (5) holds is shown by Table 137 in the case of poisoning by iodine.

TABLE 137

Dependence of Poisoning of the Pt Catalysis of H_2O_2 by Iodine upon the Iodine Concentration

$\alpha = 3{\cdot}28$; $\beta = 0{\cdot}611$; (Pt) = 2·0 mg. per litre ; $t = 25°$

c (micromol per l.).	t_c (obs.).	t_c (calc.).
$\frac{1}{\infty}$	7·7	—
0·1	13·9	13·9
0·2	19·8	17·2
0·4	21·6	22·2
1·0	33·8	33·0
2·0	48·4	46·3
4·0	65·7	66·7

Many details in the behaviour also speak in favour of an adsorption. The poisoning is often reversible. By washing out, the poison may be removed from the platinum and the degree of poisoning lowered. Further, the order in which poison and H_2O_2 are added to the sol is of consequence. If the poison is added first, and then the H_2O_2, the poisoning is much stronger than when it is added together with the H_2O_2 or even after mixing sol and H_2O_2. The poison is present in such small concentration that it cannot afterwards displace any other substance from the surface of the platinum; it is however adsorbed without hindrance when it meets the surface alone.

It depends therefore not upon a displacement of the H_2O_2 by the poison, but probably, if we apply the view which O. Warburg has employed in other cases (cf. p. 232), upon the occupation of active parts of the surface with formation of loose complex compounds. It then becomes intelligible why substances such as hydrocyanic acid and carbon monoxide are poisons, although they are only feebly adsorbed. It is true that their adsorption upon platinum has never been expressly measured; but with a substance so soluble in water as hydrocyanic acid, for example, the slight adsorption measured on charcoal may be assumed as probable for other adsorbents as well. In the case of the cystine oxidation, the excessively small concentration of poison which was active could be explained on the grounds that only the points of the charcoal covered with iron were occupied by the poison. Here in the case of metal sol catalysis it is not necessary to suppose that particularly favourable places for catalysis depend upon the presence of any foreign metal—even if this possibility were not *a priori* excluded; for the metal itself may give complex compounds with the poison. The smallest concentrations of poison required are, according to Table 137, still so large, that the number of poison molecules present in the solution is much greater than the number of Pt atoms at the surface of the Pt particles. A considerable part of the Pt surface can therefore still be coated with poison, even if we assume a very slight adsorption of the poison. The concentration of poison is therefore not so small that one need only regard a small part of the Pt surface as active.

Certain facts, however, appear to tell in favour of the view that the whole surface of the metal is not active in the catalysis. These are the following. Some poisons (hydrocyanic acid, carbon monoxide, and others) when exposed to the action of H_2O_2 lose their poisonous action completely in course of time, whereby the Pt does not only regain its original catalytic activity, but frequently one distinctly greater. In explanation of this it is difficult to choose between the two following possibilities. Either the Pt is loosened by the reaction between the hydrogen peroxide and the compound consisting of Pt + poison, and its surface thus simply increased; or from the outset only a part and not the whole of the Pt surface is catalytically active, and it is this part which is increased by the reaction mentioned. The fact that formic acid and hydrazine, for example, increase the activity of the Pt appears to favour the second possibility.[1]

The temperature coefficient of the microheterogeneous catalysis is distinctly different from that of the macroheterogeneous; the latter amounted to about 1·28 for 10°, and thus quite corresponded to diffusion, whereas for catalysis by a Pt sol it was 1·7 for 10°, and thus corresponded more to that of a chemical reaction.

[1] *Bredig* and *Ikeda*, Zeitschr. f. physik. Chemie, **37**, 34 and 50 (1901).

The influence also of the viscosity of the solution is different for macro- and for micro-heterogeneous catalysis, but is probably to be interpreted differently. In macroheterogeneous catalysis a cane-sugar content of about 5 per cent. lowers the velocity 33 per cent., and this could be explained by the diffusion constant being inversely proportional to the viscosity. In microheterogeneous catalysis the same amount of sugar lowers the velocity by 53 per cent. It is still difficult to decide whether this depends upon a sensible adsorption of the sugar taking place on the platinum at this high concentration, H_2O_2 being thus displaced, or whether the increased viscosity of the liquid and the resulting diminution in the Brownian movement causes the adsorption equilibrium to be attained more slowly.

The extremely small amount of Pt, about 0·003 mg. per litre, which is still active appears at first very surprising. The fineness of the state of division makes this intelligible, however; for if the diameter of the particles is estimated at 100 $\mu\mu$, the amount contained in a litre has a surface of 0·1 sq. cm. Also the amount of poison which under certain circumstances is still active, is excessively small; with HCN, for example, a concentration of 0·05 micromolar = 0·0014 mg. per litre reduces the velocity to one-half with a Pt content of 2·0 mg. per litre; but as we have said, this amount of poison is not small compared with the number of Pt atoms lying on the surface of the Pt particles.

Bredig and his co-workers have also investigated the catalytic decomposition of H_2O_2 for a series of other sols; metallic sols of palladium,[1] iridium,[2] silver,[3] and gold[4]; and non-metallic of manganese dioxide[5] were used. Besides great similarities, decided differences are present, a sign, no doubt, of the high degree in which chemical processes, in the ordinary sense, are concerned. Only a few points will be noted. The influence of the OH′ ion has doubtless not merely the colloido-chemical cause alluded to above (p. 493), but it probably takes part in the reaction at the interface. Otherwise it is difficult to explain why a gold sol only accelerates the decomposition of H_2O_2 in alkaline, and not in neutral or acid solution. It is easier to understand that a MnO_2 sol, also, acts catalytically only in alkaline solution since MnO_2 is dissolved by H_2O_2 in neutral or acid solution (cf. p. 487). The maximum of effect for alkali is quite generally encountered. It is absent only in the case of an iridium sol. In this case the course of the reaction remains of the first order without sensible increase of velocity. Perhaps this sol contains such small particles that they cannot be further dispersed by the OH′ ion. That the poison effect does not solely depend upon an adsorption, but that purely chemical influences are also of importance, follows strikingly from the fact that iodine is not a poison for an iridium sol, whereas it acts as such for all other metals. The whole behaviour of iridium suggests that it is less reactive towards free halogens than e.g. platinum. Otherwise in the case of metals mostly the same substances are poisons as with platinum; only the order varies. With a MnO_2 sol these poisonous effects are not found. Here the completely different nature of the catalysing interface shows itself, and doubtless also the fact that poisoning in alkaline solution is in general more feeble.

[1] *Bredig* and *Fortner, loc. cit.* p. 489.
[2] *Brossa, loc. cit.*, p. 489.
[3] *McIntosh*, Journ. Phys. Chem. **6**, 15 (1902).
[4] *Bredig* and *Reinders, loc. cit.* p. 489.
[5] *Bredig* and *A. Marck, loc. cit.* p. 489.

Poisoning with corrosive sublimate shows with some sols the peculiarity that at very small concentrations an acceleration of the decomposition instead of a poisoning is produced. This probably depends, both in the case of gold sols and MnO_2 sols, upon the reduction of the $HgCl_2$ to mercury or Hg_2Cl_2 being strongly accelerated by alkaline H_2O_2 solutions, and the freshly formed finely divided mercury likewise catalysing the decomposition of the H_2O_2.

Of other reactions, the catalytic oxidation of chromous chloride

$$2CrCl_2 + 2HCl = 2CrCl_3 + H_2$$

by platinum has in particular been investigated, macroheterogeneously by Jablczinski,[1] and microheterogeneously by McBain[2] using a Pt sol. Here also the macroheterogeneous reaction appears to correspond to a diffusion reaction of the Nernst and Brunner type. The relation of the microheterogeneous to the macroheterogeneous reaction is again similar, the increase in velocity is greater than proportional to the increase in Pt concentration, the poisoning by the same poisons in the corresponding ratio stronger, the temperature coefficient larger. Here again it makes a decided difference whether the poisons are first added to the sol or to the reaction mixture. Here also we have the peculiar effect that corrosive sublimate strongly accelerates the oxidation in small concentration, and only inhibits it in larger; this is doubtless again caused by the reduction of $HgCl_2$ to Hg by $CrCl_2$ being favoured by the Pt sol and the finely divided mercury likewise acting catalytically. With Pt sols a strong acceleration of the reaction velocity by HCl and by chlorides is noticeable up to very considerable concentrations, and indeed, in proportion to the concentration. This clearly favours the view, as McBain has also emphasized, that in the case of a sol we are dealing with a chemical and not with a diffusion reaction; with diffusion, even with excess of a substance, its concentration should be without influence (see p. 141). The comparatively slight influence of flocculation, which McBain notes, is in agreement with the dependence of the C.V. upon the initial content of the sol referred to above (cf. p. 495).

For this reaction experiments are also available which allow of a comparison between the action of poisons on macro- and micro-heterogeneous catalysis. It appears that the poisoning is much less with the macro- than with the micro-heterogeneous. Jablczinski[3] required a concentration of hydrocyanic acid of 4 millimols per litre to reduce the velocity of the macro-reaction to one-half; McBain[4] on the other hand required one of only 0·0005 millimol per litre for the micro-reaction. This probably depends mainly on the fact that the colloidal metal adsorbs the poison more strongly.

The acceleration of the oxidation of titanous sulphate to titanic sulphate

$$Ti_2(SO_4)_3 + H_2SO_4 = 2Ti(SO_4)_2 + H_2$$

by platinized platinum foil, investigated by Denham,[5] entirely corresponds to a diffusion process.

In the catalysis of oxyhydrogen mixture by Pt sols investigated by Ernst[6] much indicates, e.g. a large independence of the pressure of the

[1] Zeitschr. f. physik. Chemie, **64**, 748 (1908).
[2] *loc. cit.* p. 489.
[3] Zeitschr. f. physik. Chemie, **64**, 756 (1908).
[4] Diss., p. 59 *et seq.*, *loc. cit.* p. 489.
[5] *loc. cit.* p. 489.
[6] Zeitschr. f. physik. Chem. **37**, 448 (1901).

gas present in excess, that the velocity of a diffusion process is being measured. It would then be a matter of diffusion through the thin layer of water which adheres to the platinum particles.[1]

Inhibition of a Reaction by Hydrophobic Sols

The inhibition of the formation of Prussian blue in an Al_2O_3 sol[2] is a good example of the manner in which the particles of a sol can inhibit a reaction. If a dilute $K_4Fe(CN)_6$ solution, and then some $FeCl_3$ solution, are added to an Al_2O_3 sol, no blue coloration is observed if the concentrations are correctly chosen. It first appears after hours or days. Here the concentrations are so chosen that if the $K_4Fe(CN)_6$ solution had been diluted with the same volume of pure water instead of with the sol, the blue coloration would have been instantaneous. This inhibition is explained as follows.[3] The formation of Prussian blue from $K_4Fe(CN)_6$ and $FeCl_3$ is a reaction which requires time.[4] In sufficiently small concentrations—0·03 millimolar for $K_4Fe(CN)_6$, and 0·9 to 4·5 mg. per litre for the ferric salt—the blue coloration appears slowly. The cause of this is probably that we are dealing with a reaction of the Fe''' ion, whose concentration in dilute solution is very small on account of hydrolysis. The concentrations used in the experiment with the Al_2O_3 sol are so large—0·11 millimolar for $K_4Fe(CN)_6$, and 273 mg. ferric salt per litre—that the blue coloration should appear quickly. But $Fe(CN)_6''''$ ions are very strongly adsorbed by Al_2O_3 particles. It may be deduced from the adsorption isothermal that under the conditions of concentration for slow production of the blue colour the content of $Fe(CN)_6''''$ ions in the solution is, on account of adsorption, of a quite different order of magnitude from 0·03 millimolar, perhaps about 10^{-15} millimolar. Now the ferric salt, in particular the Fe''' ion, is but little adsorbed by the positive Al_2O_3 particles, more particularly because they are already loaded with the $Fe(CN)_6''''$ ion. The formation of Prussian blue will not take place, therefore, at the interface, but in the main only in the solution. But in this, the concentration of $Fe(CN)_6''''$ ions is so small, that the Prussian blue is only formed very slowly, although the amount of ferric salt present is actually greater than necessary. Other anions, which displace the ferrocyanide ion from the interface in the solution, abolish the inhibition. In agreement with this explanation we have the fact that the formation of Turnbull's blue, which takes place quickly even in very small concentrations, is not inhibited by an Al_2O_3 sol.

The inhibition of the production of a red coloration by the action of OH' ions on Congo blue in presence of an Al_2O_3 sol[5] may be quite similarly explained: strong adsorption of the Congo blue by the Al_2O_3 particles,

[1] Mention should be made of the reduction by hydrogen gas of unsaturated oils containing nickel, palladium, and other metals in colloidal form as catalysts. Since liquid oils of low value may thus be transformed into solid fats suitable for food (margarine), soap-making, and other purposes, the industrial importance of this reaction is very great. Nickel reduced from organic nickel salts is used in practice as catalyst. For a full account see *C. Ellis*, "The Hydrogenation of Oils, Catalysers and Catalysis." Constable, London, 1919. [*Trans.*]

[2] *Gann*, Kolloidchem. Beiheft. **8**, 117 *et seq.* (1916); *Reitstötter*, Kolloidzeitschr. **21**, 197 (1917).

[3] *Freundlich* and *Reitstötter*, Kolloidzeitschr. **23**, 23 (1918).

[4] *Vorländer*, Ber. d. deutsch. chem. Ges. **46**, 181 (1913); Kolloidzeitschr. **22**, 103 (1918); *Vorländer* and *Häberle*, Ber. d. deutsch. chem. Ges. **46**, 1612 (1913).

[5] *Reitstötter*, Kolloidzeitschr. **21**, 199–200 (1917).

impoverishment of the solution in Congo blue, and slow reaction between this very dilute solution and the OH' ions.

To the same group of phenomena belongs the observation of Wohler,[1] that $KMnO_4$ adsorbed on $BaSO_4$ does not react with H_2O_2, SO_2, or $(NH_4)_2S$; likewise a ferric salt adsorbed in the same adsorbent does not react with NH_4CNS or $K_4Fe(CN)_6$, nor does adsorbed NH_4CNS react with a ferric salt in solution.

2. SPECIAL PART

With hydrophobic sols, the properties which can be considered from a common point of view are already very numerous. It is mainly only the methods of preparation and the chemical properties which have to be discussed in more detail in the special part.

Lyophobic Sols with Water as Dispersion Medium

Metal Hydrosols

It is only in the case of the noble metals that we may regard the disperse phase, in water as dispersion medium, as consisting of actual metal. The base metals react so strongly with water that we must certainly assume that we obtain their oxides or hydroxides when we peptize them in a manner similar to the noble metals. No hydrosols of metals which have easily soluble oxides and hydroxides can be prepared.

Two methods of preparation may be distinguished: *condensation* and *disintegration* methods. All methods in which we start from truly dissolved substances, and, as the result of chemical reactions, cause a difficultly soluble substance to separate as a second phase, will be described as condensation methods. With the metals almost all condensation methods amount to reduction methods. With the disintegration or dispersion methods we start conversely with the dense metal, and bring it by suitable means into colloidally disperse distribution.

The condensation methods will be described first. The conditions which must be maintained in order to obtain a metal sol by reduction of a metallic salt can hardly be stated generally. According to the general view on p. 459 several stages must be passed through before the particles of a sol are formed: the formation of nuclei and sometimes their coarsening to smallest flocculi, as explained in connexion with the example of the hydrolysis of ferric chloride (see p. 456). Or also, if the nuclei may be regarded from the first as nuclei of a crystalline phase, their growth to larger particles under the influence of the velocity of crystallization. To this we must add the velocity of chemical reaction between metallic salt and reducing agent. We know too little concerning all these velocity processes, concerning the effect of temperature, foreign substances, and so on upon them, to be able to explain from point to point the exact directions for the preparation of a colloidal solution. It is doubtless quite generally favourable to its formation, when the second phase separates quickly in many small nuclei, and when no strongly flocculating ion is present.

[1] Zeitschr. f. anorg. Chemie, **59**, 203 (1908).

Gold Sols obtained by Reduction

Colloidal gold solutions are particularly well known from the investigations of Zsigmondy[1] and his co-workers. With these he was also able to explain qualitatively to a large extent the conditions of formation. The latter are here in so far simpler, in that we may certainly reckon with crystalline particles in the case of gold (cf. p. 413). Of the succession of processes (cf. p. 459), therefore, only three or four need be taken into account. These are, apart from the actual reduction velocity, the velocity of formation of nuclei, the velocity of crystallization of these nuclei, and the coagulation velocity of the resulting particles. If it is required to produce sols as fine-grained as possible, a large crystallization velocity is disadvantageous, a large velocity of formation of nuclei advantageous. The latter was shown directly. A gold chloride solution of the same concentration, containing alkaline carbonate in excess, was reduced with various reducing agents, as shown in Table 138, and the number of particles then determined ultramicroscopically.

Table 138[2]

Importance of the Velocity of Formation of Nuclei for the Preparation of Gold Sols

Reducing Agent.	No. of Particles in 1,000 μ^3	Duration of Reduction.	Appearance of Sol.
Ethereal phosphorus solution	120,000	Few minutes	Bright red, completely clear.
Formaldehyde solution	5,000	2″	,, ,, ,,
Hydroxylamine . . .	5	10″	Turbid blue suspension.

As we see, in the reduction with the ethereal solution of phosphorus and with formaldehyde, a large number of particles corresponds to the production of red, stable sols, containing, therefore, small particles, while with hydroxylamine, corresponding to the small number of particles, the sols are blue, cloudy, and not very stable. From this alone it cannot be concluded that the velocity of formation of nuclei is large with the ethereal phosphorus solution and with the formaldehyde, and small with hydroxylamine. It is of course conceivable that the velocities of formation of nuclei are the same and not too large, the crystallization velocities on the other hand very different. With hydroxylamine it is perhaps very large; the reduced gold would then exclusively serve the purpose of coarsening the nuclei first formed, and not of forming new nuclei. With other reducing agents, on the other hand, the crystallization velocity would be small; hence only a small part of the gold would serve to coarsen the particles first formed, the greater part would give new nuclei, even in the further progress of the action, on account of the sufficiently large velocity of formation of nuclei.

[1] Particularly *Zsigmondy*, Lieb. Ann. **301,** 30 (1898); "Zur Erkenntnis der Kolloide," Jena, 1905, p. 97; Zeitschr. f. physik. Chemie, **56,** 65 and 77 (1906); Zeitschr. f. Elektrochemie, **12,** 631 (1906); "Kolloidchemie," 3rd Ed., Leipzig, 1920, p. 144 *et seq.*; *Dörinckel*, Zeitschr. f. anorg. Chemie, **63,** 344 (1909); *Hiege, ibid.* **91,** 145 (1915); *Westgren, ibid.* **93,** 151 (1915); *Reitstötter*, Kolloidchem. Beiheft. **9,** 222 (1917).

[2] *Zsigmondy*, "Kolloidchemie," 3rd Ed., Leipzig, 1920, p. 145.

Corresponding to the mutual independence of the velocity of formation of nuclei and the crystallization velocity (see p. 326), Zsigmondy found means of influencing them separately. Thus ammonia and particularly potassium ferro- and ferri-cyanides very greatly reduce the velocity of formation of nuclei in the formaldehyde process.[1] With a concentration of potassium ferricyanide of $7{\cdot}6 \times 10^{-3}$ millimolar it becomes practically zero. The crystallization velocity is practically unaltered, for if a solution containing gold nuclei (cf. p. 399) be added to a reduction mixture of this kind containing ferricyanide and not crystallizing out spontaneously, the nuclei grow, and a sol with larger gold particles is finally formed, provided that an extraordinarily large number of nuclei have not been added. It has been found [2] that the behaviour just considered of hydroxylamine as reducing agent depends upon its likewise reducing the velocity of formation of nuclei, while nuclei added in its presence can grow further without hindrance. Hydrazine behaves like hydroxylamine. Differences in the velocity of formation of nuclei are thus actually responsible for the differences appearing in Table 138.

Conversely, substances exist which act even in small concentrations as if a solution of nuclei had been added to the reduction mixture, for example KCNS, sodium citrate, and others (these and the following statements are mainly taken from the investigations of Hiege and Reitstötter). We may assume that they increase the velocity of formation of nuclei, without seriously altering the crystallization velocity. They naturally favour the formation of fine-grained, red gold sols and permit the preparation of amicronic solutions.

Substances which depress the crystallization velocity likewise favour the formation of fine-grained sols without sensibly altering the velocity of formation of nuclei. These are, in the first place for the formaldehyde method, hydrophilic colloids such as gelatine, soap, etc., which depress similarly the crystallization velocity of salts (cf. p. 337). Then KBr and KI in large concentration inhibit, curiously enough, the separation of the gold from the reduction mixture, and this inhibition remains even if a solution of nuclei be added to the mixture, a sign that we are dealing with a reduction of the crystallization velocity. Why these substances in not too high concentration favour the formation of fine-grained sols, is evident. Nuclei are formed during the whole separation process, without the nuclei first formed enlarging sensibly by growth. The gold serves mainly only the purpose of forming many small gold particles.

Altogether, the ratio $\frac{\text{velocity of formation of nuclei}}{\text{velocity of crystallization}}$ must be as large as possible, if we wish to obtain very fine-grained sols. In general we may also say that a long duration of the separation is favourable to the formation of such sols. For if we regard the velocity of formation of nuclei as constant and of medium value, a longer duration of separation means nothing else than a slow crystallization. With a very large velocity of formation of nuclei practically all the gold might separate in the form of fine particles even with a very short duration of separation. Rise of temperature, as of concentration, is generally disadvantageous in the preparation of gold sols by reduction, apparently because they increase the crystallization velocity, while the velocity of formation of nuclei is not altered, or not to a corresponding degree.

[1] *Hiege, loc. cit.* p. 502. [2] *Reitstötter, loc. cit.* p. 502.

The fact that reduction mixtures can be prepared in which practically no nuclei arise, while they grow all the same, makes it possible to determine the size of the particles contained in a solution of nuclei. The number of particles simply remains unaltered after the solution of nuclei has been poured into the reduction mixture. If ν_K is the number of particles in 1 cc. of the solution of nuclei, v_K their volume, ν_S the number of particles in 1 c.c. of the final sol, as determined ultramicroscopically, and v_S the volume of the sol, then

$$\nu_K = \frac{\nu_S v_S}{v_K}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Since the total amount of gold is known, from it and ν_K the size and weight of the single particles of the solution of nuclei can be calculated. Reitstötter[1] found in solutions of nuclei prepared from the purest possible reagents with an ethereal solution of phosphorus, for particles assumed to be cubical, a length of the edge of $2\mu\mu$, corresponding to a weight of 10^{-16} mg. Smaller particles apparently no longer act as nuclei. We thus have here a method for determining the size of amicronic gold particles. The reduction mixtures in which this is possible are, as already mentioned, formaldehyde mixtures containing certain foreign substances (such as potassium ferro- and ferri-cyanide and others), and further reduction mixtures with hydroxylamine, hydrazine, and hydrogen peroxide.

That here such small nuclei, far smaller than in the case of supersaturated salt solutions (p. 324), are active, is doubtless due to the fact that in the reduction mixtures of gold solutions we are dealing with extraordinarily high supersaturations. This is obvious when we consider how small is the true solubility of gold. According to Ostwald's formula (1, p. 322) the radius r of the smallest crystal which still acts as a nucleus is very small for very large supersaturations, that is for very large values of $\frac{L_\omega}{L}$.

The following details may be given of the various methods of preparation.[2] In the formaldehyde and the phosphorus methods we start from alkaline solutions of gold salts. These are prepared from 120 c.c. of pure water—distilled through a silver condenser and kept in Jena glass vessels—to which are added, with warming, 2·5 c.c. of a gold chloride-HCl solution (6 g. $HAuCl_4 \cdot 4H_2O$ in 1 litre of water) and 3 c.c. of a pure K_2CO_3 solution (0·18 N). In the formaldehyde method the solution is heated to boiling and 3 to 5 c.c. of a formaldehyde solution (0·3 c.c. of the formol of commerce in 100 c.c. of water) added. The following are the reactions which take place[3]:—

$$HAuCl_4 + 2K_2CO_3 + H_2O = Au(OH)_3 + 2CO_2 + 4KCl,$$
$$2Au(OH)_3 + K_2CO_3 = 2KAuO_2 + 3H_2O + CO_2,$$
$$2KAuO_2 + 3HCHO + K_2CO_3 = 2Au + 3HCOOK + H_2O + KHCO_3.$$

Since the resulting CO_2 is disadvantageous to the formation of fine-grained sols, the boiling of the solution must continue so long that it is certainly removed (Naumoff[3]). The red sols thus obtained contain mainly submicrons and are fairly evenly grained. If we wish to obtain amicronic sols in this way, the reduction mixture must be greatly diluted and the sol concentrated by evaporation. The method depends upon the high rate of

[1] Kolloidchem. Beiheft. **9**, 245 (1917).
[2] See particularly *Zsigmondy*, "Kolloidchemie," 3rd Ed., p. 149, *et seq.*
[3] Naumoff, Zeitschr. f. anorg. Chemie, **88**, 38 (1914).

formation of nuclei in reduction mixtures containing formaldehyde under the conditions of experiment (cf. Table 138). The impurities which are disadvantageous—silicates, Fe_2O_3, etc., arising from the glass—act either because they lower the velocity of formation of nuclei itself, or coagulate the particles.

In the phosphorus method [1] the same gold solution containing K_2CO_3 is reduced by an ethereal phosphorus solution, usually in the cold. $\frac{1}{2}$ c.c. of an ethereal solution of phosphorus, prepared by diluting a saturated solution five times, is used. The sol appears in the course of about 24 hours. Brown, blue or violet tints which depend upon the temporary formation of aurous oxide appear before the final red colour. The ether can be removed by boiling. The sols are amicronic, contain particles of a diameter of 1 to 3 $\mu\mu$, and are suitable, as frequently mentioned, as solutions of nuclei.

By aid of them Zsigmondy and his co-workers have worked out a series of methods distinguished by the fact that they allow very evenly-grained sols of practically any size of particle to be obtained. The fundamental principle of this method has already been discussed (p. 399). Here we need only add that the mixture of the solutions of gold salt and of nuclei may be reduced by very diverse reducing agents; formaldehyde, hydroxylamine, and hydrazine have proved of value. With formaldehyde and hydroxylamine a gold solution containing alkali carbonate must be used; with hydrazine this is not necessary, and faintly acid red gold sols may be obtained. Without a solution of nuclei coarse suspensions or blue gold sols are obtained according to the conditions of temperature and alkalinity, as earlier prepared by Gutbier.[2] With the low rate of formation of nuclei in the presence of hydroxylamine and hydrazine, the number of nuclei is always too small to give fine-grained sols; the C.V. preponderates entirely and allows a comparatively small number of nuclei to grow very strongly.

It may be further remarked that in all these methods the solution of gold salt employed is very dilute, and its concentration must be so chosen that, as the gold is formed, the C.V. is not too great, so that too large particles are formed. We are not here dealing with methods in which the substance separated as second phase can be re-peptized.

A similar systematic investigation of other reducing agents would render it intelligible why some have hitherto led to red, others only to blue sols, and how they should be altered so as to give fine-grained sols.[3] Red sols have been obtained in particular with acetylene,[4] carbon monoxide,[5] and tannin.[6] Acetylene is a very convenient reducing agent; it may be led through the aqueous solution of gold salt, or an ethereal solution of $AuCl_3$ may be allowed to drop into acetylene water. In the case of gold sols

[1] *Faraday* (*loc. cit.* p. 1) was the first to prepare gold sols with ethereal solution of phosphorus.

[2] Zeitschr. f. anorg. Chemie, **31,** 448 (1902); **32,** 106 (1902).

[3] On the preparation of colloidal solutions *Svedberg* should be repeatedly consulted: "Die Methoden zur Herstellung Kolloider Lösungen," Dresden, 1909.

[4] *Blake,* Amer. Journ. of Science (4), **16,** 381 (1903).

[5] *Donau,* Wiener Monatsheft, **26,** 525 (1905).

[6] *Wo. Ostwald,* "Die Welt der vernachlässigten Dimensionen," Dresden and Leipzig, 1915, p. 22. Concerning gold sols formed by the illumination of suitable gold-salt solutions, see *Vanino,* Kolloidzeitschr. **2,** 51 (1907); *Hartwagner, ibid.* **16,** 79 (1915); *Herstad,* Kolloidchem. Beiheft. **8,** 399 (1916).

formed by treatment with a hydrogen flame,[1] it is essentially a reduction by nitric oxide.[2]

The experimental conditions under which the various kinds of blue sols arise (cf. p. 385) are not yet known. In the preparation of gold sols a blue colour may also at first appear, since aurous oxide is first formed; upon further reduction such sols pass into red.

The gold sol may be taken as the prototype of a hydrophobic sol, in which the hydrophilic properties are very greatly suppressed. As hydrophobic sol with small content of disperse phase it shows properties, such as density, viscosity, etc., which are scarcely different from those of water. The properties arising from the micellæ, such as Brownian movement, colour, Tyndall effect, and so on, are very distinct. The change of the red colour to blue, in consequence of the coarsening of the particles, follows throughout the laws of coagulation discussed above (p. 418).

The gold sols are more stable in alkaline than in neutral or even faintly acid solution. Alkaline gold sols stand heating and evaporation without undergoing any alteration worth mentioning, while neutral or acid sols flocculate or at least change colour. Thus the acid gold sols of Donau prepared with carbon monoxide turn blue when shaken in a test-tube closed by the finger, also in the presence of a liquid, such as benzene, not miscible with water (Zsigmondy; cf. p. 483); alkaline sols prepared by the formaldehyde method do not. This depends upon the fact that small amounts of proteins from the finger give in acid solution colloidal kations which strongly coagulate the negative Au particles; the colloidal anions, which preponderate in alkaline solution, do not (see p. 583).

Upon dialysing an alkaline sol the alkali above all is removed.[3] The sol becomes faintly alkaline and finally neutral; at the same time the kataphoretic migration velocity and also the F.V. increase.[4] This is a sign that the alkali concentration in the original sol is greater than corresponds to the maximum of the ζ, c curve; this maximum is approached with decreasing OH'-ion concentration. With very long continued dialysis the F.V. apparently falls again, because the maximum is passed.

With fresh gold sols the presence of residues of the reducing agent, e.g. formaldehyde or other reducing substances such as formic acid, produced during the reduction, exerts an influence on their behaviour. Thus it was observed in fresh alkaline gold sols that corrosive sublimate, otherwise ineffective as a coagulator on account of its slight electrolytic dissociation, produces in small concentrations the change from red to blue.[5] Since both alkali and the presence of a reducing agent appear to be necessary, this effect should depend upon the sublimate being reduced to a mercurous compound, which is more strongly dissociated and hence flocculates more strongly.[6]

The phenomenon is often described, both in the case of Zsigmondy and Bredig gold sols, of moulds forming colonies in them, upon the mycelium of which the gold collects. That this even happens with the Bredig sols,[7] which from the start contain

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[1] *Donau*, Kolloidzeitschr. **16**, 81 (1915).
[2] *Halle* and *Pribram*, Ber. d. deutsch. chem. Ges., **47**, 1398 (1914).
[3] *Herstad, loc. cit.* p. 505.
[4] *Galecki*, Zeitschr. f. anorg. Chemie, **74**, 196 *et seq.* (1912).
[5] *H. Morawitz*, Kolloidchem. Beiheft. **1**, 323 (1909).
[6] *Herstad, loc. cit.* p. 505.
[7] "Anorganische Fermente," Leipzig, 1901, p. 30. Further *Liversidge*, Chem. News, **62**, 277, 290 (1890).

no organic compounds, appears curious. If it should prove correct that such colonies of mould appear more easily in a gold sol than in an aqueous solution of the same composition but containing no gold, one might perhaps explain this according to Nathansohn as follows. Moulds need for their life processes small amounts of organic matter which are obtained from the air. These collect to some extent in the gold sol since they are continually adsorbed by the gold particles, whereby a stronger diffusion gradient of the substances in question from the air is brought about. For the collection of the gold in the mycelium it is essential, according to an investigation by Frl. v. Plotho,[1] that the proteins of the mycelium are positively charged as a result of a suitable $H^{\cdot}$ ion concentration, and, in accordance with the above-described interaction (p. 481) between colloid particles and oppositely charged adsorbent, take up the negative gold particles.

From the appearance of such colonies of mould the fact must be distinguished, that certain moulds are able to reduce solutions of gold salts to gold sols. According to Hartl[2] aspergillus oryzæ has an especial power of reducing dilute solutions of gold chloride.

The disperse phase content of a gold sol may be determined by flocculating the sol with HCl, allowing the flakes to settle, siphoning off the liquid, evaporating to dryness, and weighing. The sol may also be deposited on platinum foil by kataphoresis and weighed. It must be remembered that the gold is not always present entirely as disperse phase, but that a part (up to 10 per cent.) may be present as gold salt; in the liquids from which the gold has been separated, it has sometimes been possible to obtain a fresh gold sol by reduction.[3] A part of this salt no doubt plays the part of active electrolyte.

Sols of other Metals prepared by Reduction

The sols of other noble metals, which are prepared in a similar manner by reduction without protective colloids, have been up to the present less thoroughly investigated.

In the case of silver the sol prepared by reduction of Ag_2O by hydrogen is noteworthy, and its properties have been discussed earlier (p. 374).[4] It would still be very desirable to know more accurately the physical properties, such as size and shape of the colloid particles, etc., of a sol whose chemical composition is so exactly known. It might likewise be possible to conclude, from investigations of its catalytic action, which constituents of the micellæ are of importance. Other silver sols have been prepared by reduction with hydrazine hydrate,[5] catechol,[6] pyrogallol.[7] They are coloured brown-red to olive-green.

The blood-red, shining-brown or greenish-brown silver sols, prepared by the method of F. Wöhler[8] and Muthmann[9] and Carey Lea,[10] have striking properties. Muthmann, extending earlier experiments of F. Wöhler, reduces silver citrate in the warm with hydrogen, and peptizes the resulting

[1] Biochem. Zeitschr. **110,** 1 and 33 (1920).

[2] "Beiträge zur Chemie des Goldes und des Wismuts," Diss., München, 1906. See also *Liversidge, loc. cit.* p. 506.

[3] *Steubing, loc. cit.* p. 383.

[4] *Kohlschütter, loc. cit.* p. 372.

[5] *Gutbier,* Zeitschr. f. anorg. Chemie, **32,** 350 (1902).

[6] *Henrich,* Ber. d. deutsch. chem. Ges. **36,** 615 (1903).

[7] *Garbowski, ibid.* **36,** 1215 (1903).

[8] Lieb. Ann. **30,** 1 (1839).

[9] Ber. d. deutsch. chem. Ges. **20,** 983 (1887).

[10] *Carey Lea* and *Lüppo-Cramer,* "Kolloides Silber und die Photohaloide," Dresden, 1908; see also *E. A. Schneider,* Ber. d. deutsch. Chem Ges. **24,** 3370 (1891); **25,** 1281 (1892).

precipitate with dilute ammonia. Carey Lea reduces silver nitrate solution with a ferrous sulphate solution and peptizes the reduction product with water. The disperse phase of the Carey Lea sol contains about 97 to 98 per cent. of silver. The remainder consists of iron salts and organic reaction products, which, doubtless themselves colloidal, act in a certain sense as protective colloids. According to the behaviour towards electrolytes this sol is however thoroughly electrocratic (cf. p. 591); on the other hand, it corresponds to a content of substances similar to protective colloids, that the coagulated flakes of these sols are readily re-peptized, which is otherwise not the rule with metal sols. The flocculated disperse phase has a very different colour, brown, green, red or gold, according to the conditions of reduction. This doubtless depends upon the same causes as were suggested in the case of gold (p. 385), namely the various sizes and forms of the silver particles. Under certain circumstances, the presence of different amounts of foreign substances will possibly also not be without influence. That the silver in this sol is present in a special allotropic form, as Carey Lea at first supposed, is improbable, and could be decided by the method of Debye and Scherrer (p. 332). Whether, in the transformation of the variously coloured forms into one another and finally into crystalline silver, the same regularities hold which were found for the coarsening of flocculi and the reversal of adsorption (p. 453), still remains to be investigated. Red sols are the most highly disperse; but they are also the least pure.

If chlorine water is added to Carey Lea or Wöhler-Muthmann sols, we obtain colloidal solutions of the so-called *photochlorides*, colloidal mixtures of silver and silver halides.[1] They will be discussed more fully later (p. 803) on account of their notable properties; for the exposed silver halide grains of the photographic film consist of them, and they are sensitive to colour.

It is said that the sols of copper and mercury obtained by reduction are very unstable. By reduction of copper sulphate solution with hypophosphorous acid at 70–80° Gutbier [2] obtained a sol, the particles of which, as judged by the colour, actually consisted essentially of the metal, for it was blue by transmitted and bronze by reflected light. He prepared a mercury sol by reduction of a suspension of Hg_2O or HgO in water with hydrazine hydrate.[3]

The sols of palladium and platinum obtained by reduction are, on the other hand, more stable. For example, the chlorides have been reduced in alkaline solution by formaldehyde and then dialysed.[4] With platinum other reducing agents such as hydrazine hydrate,[5] catechol [6] and others,[7] have been tried with success. The sols are brown to black.

McCoy [8] observed the appearance of colloidal solutions of mercury under circumstances worthy of note. He made tetramethyl-ammonium amalgam by electrolysing an alcoholic solution of $N(CH_3)_4Cl$ with a silver anode and mercury cathode. The amalgam is decomposed by water with the formation of a Hg sol, which is at first black and then grey.

[1] *Baur*, Zeitschr. f. physik. Chemie, **45**, 613 (1903).
[2] Zeitschr. f. anorg. Chemie, **32**, 355 (1902).
[3] *Gutbier*, Zeitschr. f. anorg. Chemie, **32**, 353 (1902).
[4] *Lottermoser*, "Anorgan. Kolloide," 1901, pp. 33 and 34.
[5] *Gutbier*, Zeitschr. f. anorg. Chemie, **32**, 352 (1902).
[6] *Henrich*, Ber. d. deutsch. chem. Ges. **36**, 614 (1903).
[7] *Garbowski*, *loc. cit.* p. 507.
[8] *McCoy* and *W. C. Moore*, Journ. Amer. Chem. Soc. **33**, 273 (1911); *McCoy* and *West*, Journ. Phys. Chem. **16**, 261 (1912).

Metallic Hydrosols prepared by Peptization

All other methods for the preparation of metallic hydrosols differ from the foregoing reduction methods in that they proceed from the dense metal. We may perhaps distinguish three different methods ; disintegration in the electric arc, disintegration by electrolysis, and peptization by the action of chemical reagents. The production of metallic sols by the action of ultra-violet light or X-rays is also a peptization by chemical reagents.

Disintegration in the electric arc, and the sols prepared in this way, are best known. Bredig [1] was the first to elaborate this method and to use it extensively. He placed two thick wires (best about 1 to 2 mm. thick) of the metal to be disintegrated under water and struck an electric arc between them ; a direct current of 4 to 10 amperes at 35 to 50 volts was used. The dispersion medium is placed in a crystallizing dish, which it is advisable to cool with ice (see Fig. 115). In place of pure water it is advantageous to use a dilute solution of alkali (0·001 molar), in particular an alkali with a univalent inorganic kation, NaOH or KOH. The favourable effect of the alkali depends upon the charging, and hence peptizing, action of dilute solutions of OH' ions already frequently referred to ; provided, naturally, that the metal to be dispersed tends to charge itself negatively. A certain skill is required to so hold the electrodes that they do not melt together and yet are not too far apart. Thick clouds of the metal must rise from the electrodes. These must be quickly and uniformly distributed in order that local overheating may be avoided as much as possible. Burton [2] prefers to direct the electrodes by a mechanical arrangement instead of by hand. Stable hydrosols of silver, gold, and the platinum metals are obtained by this method.[3] Mercury sols may also be prepared with the help of a direct-current arc,[4] by using as one electrode a jet of mercury, as the other a pool of the same, into which the jet falls through the dispersion medium. It is important that the dispersion medium be kept at a sufficiently low temperature by means of a cooling coil in the liquid ; the presence of peptizing agents, ammonium salts or citrates, is advantageous.

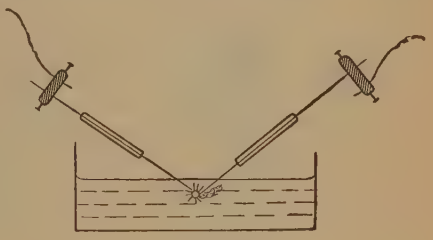


Fig. 115.

The Bredig method fails in the case of organic solvents, since too great decomposition and separation of carbon occurs. A systematic investigation by Svedberg [5] has however increased the effectiveness of the arc method to such an extent, that he even succeeded in producing sols of the alkali metals in liquids such as pentane or ethyl ether. First of all, it proved to be advantageous to make the size of the spark as small as possible. Svedberg

[1] Zeitschr. f. angew. Chem. 1898, p. 951 ; "Anorganische Fermente," Leipzig, 1901.
[2] Phil. Mag. (6), **11**, 425 (1906).
[3] A rhodium sol was made by Lancien, according to Bredig's method, Compt. rend. **153**, 1088 (1911).
[4] *Nordlund*, "Experimentelle Studien über Quecksilbersole, die aus metallischem Quecksilber hergestellt sind." Diss., Upsala, 1918, p. 30 *et seq.*
[5] Ber. d. deutsch. chem. Ges. **38**, 3616 (1905) ; **39**, 1705 (1906) ; Nov. act. reg. soc. scient. Upsala (4) **2**, No. 1 (1907).

effected this by not allowing the arc to pass directly between the electrodes, but by using the metal to be dispersed in the form of foil, and distributing it in pieces between two fixed electrodes. These electrodes need not be of the same metal, but may consist of any metal, such as aluminium or zinc, which is difficult to disintegrate. At a potential difference of 110 to 120 volts a current of 20 to 50 milliamps. passes through the liquid; a lively play of sparks occurs between the fragments of metal. These sparks are very small and the heating very much limited spatially, since the sparks between the fragments of metal, which move about, continually change their position.

Still more effective is a second experimental arrangement, in which the oscillatory discharge from an induction coil is used instead of direct current. Svedberg investigated the essential conditions with an arrangement as represented in Fig. 116. B is an induction coil. The capacity of the two Leyden jars is connected in parallel with the spark-gap A; between A and C self-induction coils and resistances may be introduced when it is required to determine their influence upon the disintegration. It was found that the disintegration is most favourable, and the decomposition of the organic liquid smallest, when the capacity is chosen as large as possible, and the spark-length, the resistance, and the self-induction as small as possible. As far as the behaviour of the electric arc in liquids is known, these conditions indicate sparks of as short a duration as possible, frequently interrupted, and which generate a considerable amount of heat.

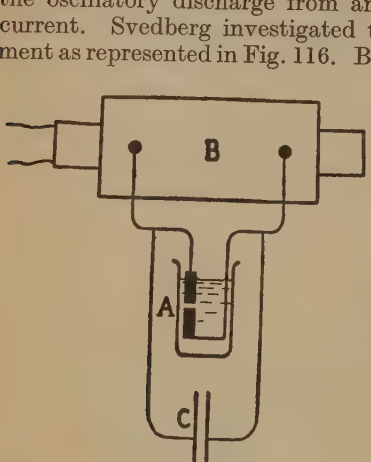


Fig. 116.

The phenomena which take place in this disintegration of metals are of a fairly complicated nature; it is a question both of a vaporization and subsequent condensation of the metal, and of a local melting and disintegration of the molten metal. Benedicks [1] has in particular proved the existence of the latter phenomenon and investigated it more closely. With strong oscillatory discharges he found small craters on the electrodes, similar to those which can be produced by blowing a stream of hot air from a fine nozzle on to a plate of paraffin wax. He explains their production as follows. The metal melts at the point where the spark strikes it; as soon as the latter is interrupted, the dispersion medium streams violently in and hurls the metal in fine drops out of the crater. A metal should give a greater yield of disintegrated particles, the smaller its total heat of fusion—heat necessary to heat the metal to melting-point and to melt it—and the smaller its conductivity for heat; for if the latter is great, the heat is conducted away so rapidly that a considerable degree of melting does not occur. In actual fact, the order of the metals when arranged according to their difficulty of disintegration, as found by Svedberg, corresponds entirely to expectation; the yield of dispersed metal is the greater, the smaller the total heat of fusion and the conductivity for heat.

[1] Ark. f. Matem., Astron. och Fys. **8**, No. 7 (1912).

This phenomenon is not however alone responsible for the disintegration. A part of the metal is always evaporated by the sparks, and this evaporation preponderates as soon as the discharges are weak. No crater is then observed because insufficient heat is communicated to melt such large quantities of the metal, but of course a smaller amount will always be vaporized directly at the point where the very hot spark meets the metal. Vaporization naturally depends upon properties of the metal other than those concerned in the formation of craters mentioned above. It appears to depend especially upon the work required to bring the metal into the state of vapour against the pressure of the liquid; for one has the impression that under similar conditions equiatomic amounts of different metals are disintegrated. The order of the metals as regards the difficulty of disintegration depends therefore on the strength of the discharge employed.[1] It is extremely likely that, as follows from a discussion between Kutscherow[2] and Benedicks,[3] this vaporization is just as important for the production of the colloidal solution, as the phenomenon investigated by Benedicks, in so far as in the latter case coarser particles, microns, arise, while with vaporization, in spite of the smaller amount of metal disintegrated, submicrons and amicrons are preferentially formed. In favour of this we have amongst other things the circumstance that, according to Bredig and Ikeda,[4] the catalytic activity of a platinum sol prepared with a current of 4 to 6 amperes is considerably greater than that of one of the same platinum concentration prepared with a current of 8 to 12 amperes. The supposition at once occurs that the finest particles have the greatest catalytic activity, and that these are formed more freely by vaporization alone with the weaker discharge, than with the stronger.

In any case it follows from the conditions of preparation that sols obtained by electrical disintegration are more polydisperse than those obtained by reduction. The micellæ are in part so coarse that they settle rapidly or can be readily filtered off; gold sols are generally blue or violet, and particular care has to be taken, even if alkali is used, to obtain red sols by disintegration. Against this disadvantage of a lesser uniformity in the size of the particles we have the advantage that the sols are in general purer than those obtained by reduction. It is true that we must not simply assume that a platinum sol prepared by electrical disintegration contains nothing but water and platinum (and perhaps some alkali). It has already been shown on p. 375 that silver sols obtained by disintegration contain a certain amount of silver oxide; a similar state of affairs will hold to a greater or lesser degree for all other metal sols obtained by disintegration, and especially so, the less noble is the metal in question. Bredig[5] obtained very unstable sols by the disintegration of cadmium wires; one will be inclined to regard them rather as oxide than as metal sols. For the copper sol obtained by Paine[6] in the same way behaves to a great extent like an oxide sol, as does also the iron sol investigated by Malarski.[7]

[1] In agreement with this is the fact that in the disintegration of metals by the wave-current (Poulsen) arc [*Svedberg*, Physik. Zeitschr. **15**, 361 (1914); *Börjeson* and *Svedberg*, Kolloidzeitschr. **25**, 154 (1919)] the order is a different one than for the oscillatory discharge.

[2] Kolloidzeitschr. **11**, 165 (1912).

[3] *Ibid.* **11**, 263 (1912).

[4] Zeitschr. f. physik. Chem. **37**, 2 (1901).

[5] Zeitschr. f. physik. Chem. **32**, 127 (1900); "Anorganische Fermente," p. 33 (1901).

[6] *loc. cit.* p. 416.

[7] *loc. cit.* p. 392.

This oxidation is doubtless important for the catalytic activity of a platinum sol; this has not yet been investigated in detail. In other respects this is the best known of the sols obtained by disintegration. In all its properties it is the prototype of a hydrophobic sol. It has also been observed that it ages, which is shown by an initial change in its catalytic properties; later, it remains for a long time practically unchanged as regards catalytic activity (see p. 456). The analytical determination of the Pt content [1] is carried out by coagulating with sulphuric acid, filtering, igniting, and weighing. If a small amount of platinum was dissolved in the liquid filtered off—perhaps originally present as oxide of platinum ?—this can be precipitated with H_2S and treated further with the remaining Pt.

Mercury sols [2] have a reddish-brown colour when they are rich in amicrons and submicrons; if their colour is more grey, the droplets are larger It is curious that in contrast to the other sols of the noble metals, they are not negatively, but as a rule positively charged. The sols dispersed by a direct current contain mercuric oxide in sensible amount. They therefore behave rather as mercuric oxide sols. The flocculation values do not show so clearly the usual regularities. Perhaps this depends upon the sols being, as the low flocculation values show, fairly unstable, so that a rapid coagulation is in reality being observed; that it is not actually "rapid" might be caused by the comparatively low content of the sol in disperse phase (cf. p. 434).

Statements exist according to which metal sols may be obtained by electrolysis under suitable conditions. Billiter [3] states that in the electrolysis of very dilute $AgNO_3$ and $HgNO_3$ solutions brown clouds which he regards as colloidally dispersed silver and mercury respectively enter the solution at the anode. With silver this is certainly not the case; for according to experiments by Haber [4] the turbidity dissolves readily in ammonia. It is here doubtless a question of a colloidal solution of silver oxide. In the case of both metals Haber was able to prove the presence of small amounts of ammonia in the solution, so that he believes that also in the case of mercury we are dealing with the complex black compounds which have been obtained by the action of small amounts of ammonia on dilute $HgNO_3$ solutions (mercurius solubilis Hahnemann).

Mercury sols may be obtained by very direct methods of peptization. According to Nordlund,[5] only small amounts of colloidal mercury are obtained by forcing mercury in the finest spray from a tube into water containing a suitable peptizing electrolyte (ammonia, ammonium salts, citrates). It is much more effective to shake mercury with such aqueous solutions. This surprising difference is explained as follows. In the case of the spraying jet the mercury is subdivided at the expense of external mechanical energy; in the case of shaking the essential part of the phenomenon is, that many drops of the solution are formed in the mercury, and surround themselves with a thin skin of mercury, which, when it bursts, produces drops much finer than those produced by spraying. This observation also favours the view that in disintegration in the arc the mechanical-thermal effect emphasized by Benedicks (p. 510) mainly produces coarse particles; for, in the

[1] *Bredig* and *Müller v. Berneck*, Zeitschr. f. physik. Chemie, **31**, 272 (1899).
[2] *Nordlund, loc. cit.* p. 509.
[3] Ber. d. deutsch. chem. Ges. **35**, 1929 (1902).
[4] Zeitschr. f. Elektrochemie, **8**, 551 (1902).
[5] *loc. cit.* p. 509.

rush of the liquid into the craters filled with molten metal, it is rather a matter of the dispersion of drops than of the bursting of lamellæ.

Evaporation, which according to this is the main cause of colloid formation, may also be directly applied to the production of mercury sols.[1] Nordlund caused mercury to boil violently and led the stream of vapour into cooled water which contained the peptizing electrolytes mentioned. The colloidal solutions obtained in this way were the richer in very small particles, the better the water had been cooled. Further, the sols prepared with citrate are negative, those with ammonia and ammonium salts positive. The special affinity of mercury for nitrogen prevents this from appearing so strange as it would otherwise—OH' ion of course usually favours a negative charge ; we may imagine that small amounts of a difficultly soluble substance of a basic nature are formed, and that we are therefore rather dealing with an hydroxide sol. According to Nordlund's measurements, these sols prepared by mechanical or thermal means proved to be more polydisperse than those prepared by electrical disintegration.

What is further known about the peptization of metals by mechanical means is frequently very uncertain. Thus the experiments of Scala and Frau Fraube-Mengarini,[2] according to which metals may be brought into colloidal solution simply by long-continued boiling with water, have proved to be incorrect.

Nordenson [3] showed that, at the best, it is a question of oxide of the metal, present from the first on the surface, being peptized, or of metal being oxidized according to the amount of oxygen present, and this oxide being then colloidally dissolved. Only in the case of silver can, under certain circumstances, a metal sol be formed in this way, since it is easily reduced from its compounds by light or dust.

The production of metal sols by the action of ultra-violet light or Röntgen rays depends, according to Nordenson,[4] upon a powerful intensification of these processes. Svedberg [5] was the first to describe the phenomenon that, when a silver plate, for example, is strongly illuminated under water with these rays, silver passes into colloidal solution. As we have said, according to Nordenson the following chain of processes is probable in the case of silver. The radiation causes the production of hydrogen peroxide, which produces a stronger oxidation of the metal than oxygen alone would produce.[6] This oxidation is perhaps accelerated by light. The oxide goes into solution, but separates again as the concentration increases, on account of its low solubility, in colloidal form, and is reduced by the rays to metal. It is only in the case of the oxidizable metals that the formation of micellæ can be observed upon long boiling or irradiation, which micellæ however, as mentioned, almost always consist of the oxide or hydroxide of the metal ; only with silver, perhaps also with mercury, does formation of the metal, by reduction, occur.

[1] *Mukhopadhyaya* [Journ. Amer. Chem. Soc. **37,** 292 (1915)] prepared sols by surrounding a platinum wire with substances such as sulphur, selenium, and arsenic, sending an electric current through the wire and causing it to glow, and so vaporizing the substance enveloping it.

[2] Kolloidzeitschr. **6,** 65, 240 (1910) ; **10,** 113 (1912).

[3] Kolloidchem. Beiheft. **7,** 91 (1915).

[4] Kolloidchem. Beiheft, **7,** 110 (1915).

[5] Ber. d. deutsch. chem. Ges. **42,** 4375 (1909) ; Kolloidzeitschr. **6,** 129 (1910).

[6] Upon an oxidation of this kind by H_2O_2 depends, according to *Siedentopf* [Kolloidzeitschr. **6,** 3 (1910)], the decolorization he observed of the micellæ of Au and Pt sols under strong illumination in the cardioid ultramicroscope.

With a number of other metals, such as zirconium,[1] thorium,[2] tungsten,[3] and others it is necessary for peptization that they be present from the outset in extremely finely divided form. Frequently, this condition is at once fulfilled, since they are obtained in the form of very fine powders by the reduction methods used for their preparation. If they are then treated with a suitable solution, which apparently also causes mainly the charging up of the particles, or the formation of protective oxides or their derivatives, they may frequently be successfully brought into colloidal solution by subsequent washing out. Thus a zirconium sol, for example, is prepared as follows.[4] By reduction of zirconium potassium fluoride by heating with metallic potassium or sodium,[5] the zirconium is obtained in the form of a fine powder, which tints the skin more strongly than soot. It is washed with alcohol and warmed cautiously with dilute acid, say acetic acid, brought on a filter and washed with cold water; at a definite point of the washing the metal commences to pass through the filter, and the product remaining on the filter may be peptized to a sol by shaking up with water. The sol is positive; it is hence clear that it is the $H^{\cdot}$ ion which charges up the particles.

In the case of tungsten the metal ground fine in a mortar is treated alternately with acid and alkali until it finally peptizes. These sols have technical importance. The metal flocculated from them may be moulded, and can be pressed into threads for the filaments of incandescent lamps. It is not necessary to start from the metal which has been peptized; the metallic powder obtained by reduction of tungsten trioxide with hydrogen may be used. In any case the filaments so made are fairly brittle. This may be improved according to a method of the firm J. Pintsch A.G. Berlin, by adding thorium oxide to the metal and heating it to incandescence in a hydrogen atmosphere. Similar coarsening processes then take place as have already been discussed (p. 330). The original extremely fine crystalline particles then unite to a single thread-shaped crystal, as was shown by X-ray photographs by Laue's method.[6]

These methods relate almost entirely to easily oxidizable metals. Hence it is extremely probable that a considerable part of the metal, if not the greater part, is present in the sol as colloidal oxide or hydroxide.[7] Of sols of this kind hardly one has been thoroughly investigated. As far as the data go, they seem to have a hydrophobic character.

Hydrosols of Other Elements

Aqueous sols of the non-metallic elements boron,[8] carbon,[9] silicon,[10]

[1] *Wedekind*, Kolloidzeitschr, **2**, 289 (1908); Zeitschr. f. anorg. Chemie, **45**, 385 (1905); *Kužel*, Austrian Patent, A 2573/06, Class 12b, April 26, 1906; see also *Lottermoser*, Chem.-Ztg. 1908, p. 311. Ref. Kolloidzeitschr. **2**, 347 (1908).

[2] *Kužel, loc. cit.* above; *Wederkind* and *Baumhauer*, Kolloidzeitschr. **5**, 191 (1909).

[3] *Kužel, loc. cit.* above.

[4] *Wedekind, loc. cit.* above,

[5] See also *Wedekind*, Lieb. Ann. **395**, 149 (1913).

[6] *R. Gross* and *Blassmann*, Neues Jahrb. f. Mineral. Geol. und Palaeontol. Beilagenbd. **42**, 728 (1919).

[7] See e.g. *Zsigmondy*, "Kolloidchemie," 3rd Ed., 1920, p. 199.

[8] *Kužel, loc. cit.* under [1]; *Ageno* and *Barzetti*, Atti d. R. Accad. d. Linc. (5), **19**, I, 381 (1910); *Gutbier*, Kolloidzeitschr. **13**, 137 (1913).

[9] *Sabbatani*, Kolloidzeitschr. **14**, 29 (1914).

[10] *Astfalk* and *Gutbier*, Kolloidzeitschr. **15**, 23 (1914).

arsenic,[1] sulphur,[2] selenium,[3] and tellurium[4] have been prepared. Condensation methods are again very important. Selenium sols are obtained by reduction of solutions of selenious acid by hydrazine hydrate (H. Schulze, Gutbier, Kruyt, and A. E. van Arkel), tellurium sols by reduction of telluric acid by the same reducing agent (Flury and Gutbier); arsenic sols by reduction of $AsCl_3$ by hypophosphorous acid in alcoholic solution and peptization of the reaction product with dilute aqueous alkali (Auger); carbon sols by dissolving cane sugar in concentrated sulphuric acid, pouring the black liquid thus obtained into distilled water and dialysing until the H_2SO_4 is removed (Sabbatani).

Of these, the selenium sols produced by reduction with hydrazine hydrate are better known: beautifully red, negative colloidal solutions of a hydrophobic character. In the preparation, the formation of nuclei and their growth may be clearly distinguished as in the case of gold sols (Kruyt and A. E. van Arkel). This fact, and further their stability and good resolvability under the ultramicroscope, renders it promising that they might be as exactly examined and used to test molecular-statistical phenomena, the C.V., and so on, as has been done by Zsigmondy with gold sols. The tellurium sols are distinguished by the variety of their colours; brown-black and steel-blue sols may be obtained. This phenomenon has doubtless causes similar to those more closely investigated in the case of gold sols (cf. p. 383).

As already mentioned (cf. p. 427), sulphur sols show, according to their type, a more hydrophobic or more hydrophilic character and hence will be considered at a later point (cf. p. 615). It has already been emphasized that a sulphur sol of v. Weimarn,[5] prepared by pouring an alcoholic sulphur solution into an excess of water, is very distinctly hydrophobic. It can, however, only be prepared very dilute and is not very stable.

Investigations could be carried out on carbon sols to see how far the adsorption phenomena, so well known in the case of charcoal, are reflected in their stability and conditions of flocculation; but the possibility must be taken into account, that the foreign substances formed in the production of this sol may so completely occupy the surface of the colloid particles as to make further adsorption comparatively slight. The fact that charcoal takes up electrolytes decidedly according to an equivalent adsorption (cf. p. 206), the majority of colloid particles otherwise according to an exchange adsorption, should increase the stimulus to elucidate the flocculation relationships of these sols, if indeed they have a hydrophobic character at all. According to present data they are negative in acid, neutral, and alkaline solution.

Electrolytic methods have proved more successful for the sols of some non-metallic elements than with the metals. Erich Müller and his co-

[1] *Auger*, Compt. rend. **145**, 718 (1907).

[2] *Odén, loc. cit.* p. 368; also extensive bibliography.

[3] *H. Schulze*, Journ. f. prakt. Chemie, **32**, 390 (1885) (Reduction of SeO_2 by SO_2); *Gutbier*, Zeitschr. f. anorg. Chemie, **32**, 106 (1902); *Kruyt* and *A. E. van Arkel, loc. cit.* p. 417 (Reduction of SeO_2 by hydrazine hydrate); *Gutbier* and *Engeroff*, Kolloidzeitschr. **15**, 193 (1914) (Hydrolysis of hydrogen selenium bromide, H_2SeBr_6).

[4] *Flury*, "Beiträge zur Kenntnis des Tellurs," Diss, Erlangen, 1903; *Gutbier*, Zeitschr. f. anorg. Chemie, **32**, 51 and 91 (1902); **42**, 177 (1904).

[5] *loc. cit.* p. 427.

workers were able readily to prepare sols of selenium [1] and tellurium [2] by using a piece of tellurium or a platinum electrode partly coated with selenium as cathode against a platinum anode in pure or faintly alkaline water. The micellæ of the two elements spread in a cloud from the cathode. This does not depend upon a direct electrical disintegration, but upon an electrolytic process, which was elucidated to a great extent in the case of tellurium. A univalent tellurium ion is first formed according to the equation

$$\mathrm{Te} + \ominus = \mathrm{Te}'.$$

This is very unstable and decomposes spontaneously into a higher and lower state of oxidation according to the equation

$$2\mathrm{Te}' = \mathrm{Te} + \mathrm{Te}''$$

with separation of finely divided tellurium. In strongly alkaline solution a deep red solution of colloidal tellurides $\mathrm{Te}_n\mathrm{K}_n$, which likewise decompose with separation of tellurium, is first formed at the cathode. Probably the relations are similar in the case of selenium.

Thorne [3] prepared colloidal carbon solutions by using carbon electrodes in dilute NaOH solutions for electrolysis. How far these were really pure carbon sols appears doubtful, since up to 16 per cent. of oxygen was contained in the disperse phase.

Carbon sols have also been prepared by disintegration with the arc under water.[4]

By electrolysis of alkaline $\mathrm{As_2O_3}$ solutions with a Pt anode and Hg cathode Lecoq [5] prepared As sols; they are unstable when protective colloids such as gum are not added.

Sols of boron [6] and silicon [6] have been prepared in a manner similar to those of zirconium, thorium, etc., by peptization of the finely divided solid metals by means of suitable peptizing agents.

Sulphide Hydrosols

The numerous sulphide hydrosols may be prepared by condensation or peptization. In the condensation method we start with a suitable dilute solution of the initial material, and treat this with sulphuretted hydrogen or with a dilute solution of an alkaline sulphide; the electrolytes which may result from the reaction are removed by dialysis. The latter process may be avoided either by taking the solutions so dilute that the concentration of the electrolytes finally remaining in solution is far below the F.V., or by choosing compounds which leave weakly dissociated end-products in the solution. Thus Lottermoser [7] prepared HgS and CuS sols by allowing $\mathrm{H_2S}$ to act upon mercuric cyanide and the copper salt of glycine respectively.

With many sulphides which dissolve in alkalis or polysulphide solu-

[1] *E. Müller* and *Nowakowski*, Ber. d. deutsch. chem. Ges. **38**, 3779 (1905).
[2] *E. Müller* and *Lucas*, Zeitschr. f. Elektrochemie, **11**, 521 (1905).
[3] Journ. Chem. Soc. **109**, 202 (1916).
[4] *Svedberg*, Ber. d. deutsch. chem. Ges. **39**, 1713 (1906).
[5] Compt. rend. **150**, 700 (1910).
[6] *loc. cit.* p. 514; especially the investigations of *Gutbier*; *Svedberg* (*loc. cit.* under [4]) prepared colloidal silicon by disintegration in the arc.
[7] Journ. f. prakt. Chemie. **75**, 293 (1907).

tions, one may also proceed by dialysing this solution; a sulphide sol remains behind in the dialyser. In this way an Au_2S_2 sol may be prepared,[1] by dissolving Au_2S_2 in a KCN or potassium polysulphide solution and dialysing. This method is entirely similar to that to be discussed later, in which hydroxide sols are obtained simply by the dialysis of solutions of metallic salts.

In the case of an As_2S_3 sol the experimental conditions are particularly clean cut, since according to the equation

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$$

no electrolytes are formed which need be dialysed away. The sol is prepared by allowing an aqueous solution of As_2O_3 to drop into sulphuretted hydrogen water through which a current of H_2S is passing; the excess of H_2S is removed by displacement with H_2, N_2, or another indifferent gas. Since the initial substances consist of weak electrolytes, the following method, which was used by H. Schulze,[2] the first investigator of this sol, may be employed to make concentrated sols. Further As_2O_3 is dissolved in the sol, fresh H_2S passed and the process repeated. Kruyt and van der Spek [3] have thus prepared As_2S_3 sols containing about 70 g. As_2S_3 per litre.

Amicronic As_2S_3 sols may also be obtained by a method that is doubtless to be regarded as a nucleus method.[4] A quantity of dilute H_2S water, insufficient for the complete transformation of the As_2O_3, is added to a not too concentrated As_2O_3 solution. In this way a large number of As_2S_3 nuclei are probably produced. These are allowed to grow by again adding at first only dilute H_2S water. Only at the finish is H_2S passed through the sol and the excess removed by hydrogen.

Of importance for the theory of the preparation of the As_2S_3 sol is the curious phenomenon, observed by Vorländer and Häberle,[5] that in large dilution and with excess of As_2O_3, the solution containing $As_2O_3 + H_2S$ remains at first colourless, and only in course of time and upon addition of acids changes into the yellow of the As_2S_3 sol. This takes place when the concentration relationships are, for example, 5 c.c. of a $\frac{1}{10}$N As_2O_3 solution + 5 to 15 c.c. of a $\frac{1}{100}$ N H_2S solution in 300 to 400 c.c. of water. Here the H_2S is bound in some manner, for by passing hydrogen through the solution, one can only remove about 11 per cent. of the H_2S in 24 hours, whilst with a pure H_2S solution under the same experimental conditions the H_2S would be completely removed in the same time.

The As_2S_3 sol is distinguished by its sensitivity to light.[6] This is not only on account of the phenomenon discussed above (p. 486), that an As_2S_3 sol becomes cloudy in the light because it is coagulated by the sulphur sol produced by light. Various dyes, such as malachite green or eosin, are bleached in 3 minutes when mixed with an As_2S_3 sol in the light of a nitra lamp (concentration of dye about 0·001 per cent.), and in diffuse daylight in the course of about half an hour. As opposed to the above-mentioned coagulation in light, the process takes place only under illu-

[1] *E. A. Schneider*, Ber. d. deutsch. chem. Ges. **24**, 2243 (1891).
[2] Journ. f. prakt. Chem. **25**, 431 (1882).
[3] *loc. cit.* p. 365.
[4] *Freundlich* and *Nathansohn, loc. cit.* p. 476.
[5] Ber. d. deutsch. chem. Ges. **46**, 1626 (1913).
[6] *Freundlich* and *Nathansohn, loc. cit.* p. 486.

mination, and not in the dark with the previously illuminated sol. We are dealing with the sensitization of a photochemical reaction by the micellæ of the As_2S_3 sol. Of further light reactions of the As_2S_3 sol, the following may be mentioned. The reaction above referred to (p. 488) with the Carey Lea silver sol is sensitive to light; the mixture of sols colours brown in the dark, doubtless owing to the formation of a mixed sulphide of As_2S_3 and Ag_2S. Under the influence of light and oxygen, the colour passes through green into dark golden yellow. Hereby a silver sulpharsenide[1] is formed. Further, As_2S_3 flocculi coagulated with purpureocobaltic chloride, $[Co(NH_3)_5Cl]Cl_2$, are turned black by light.[2]

If it is desired to prepare sulphide sols by peptization, the points of view discussed on p. 471 hold completely; one must start from as fresh and loose sulphide flakes as possible, which have been thrown down from solutions of weakly coagulating electrolytes. H_2S usually serves as peptizing agent, the excess being removed by an indifferent gas. In many cases, a sulphide containing H_2S passes into colloidal solution upon washing with water. As an example the preparation of a HgS sol may be given.[3] Loose HgS flakes are thrown down from a semi-saturated corrosive sublimate solution by H_2S, and, after repeatedly washing them with water, are peptized by vigorous mechanical stirring in water through which H_2S is passing; the excess of this gas is removed in the usual manner. One can tell from the appearance of the HgS flakes whether or not they are suited to the preparation of a sol; if they are deep black and loose, peptizing easily succeeds; on the other hand, not at all or with difficulty, if they have a somewhat metallic appearance with a greyish tinge.

In some cases it is advantageous to start from another sol or another suspension. Thus a SnS_2 sol is obtained by passing H_2S into a stannic acid sol and heating[4]; the sols of ZnS[5] and In_2S_3[5] by passing H_2S into water in which the hydroxides $Zn(OH)_2$ and $In(OH)_3$ are suspended.

The sulphide sols are to a great extent hydrophobic, although no doubt frequently less so than most metallic sols. The remarkable differences in behaviour upon coagulation by mixtures of electrolytes (cf. p. 461) may be recalled. Otherwise, the laws discussed in the General Part usually appear quite clearly.

The difference between the refractive indices of micellæ and intermicellar liquid is so great, that the ultramicroscopic picture, provided that the particles are sufficiently large, is invariably clear and sharp. In respect of colour these sols show nothing remarkable; the colour usually corresponds to that of the corresponding sulphide in the dense form.[3] Strongly marked changes during the coagulation of Ag_2S sols have, however, been observed (Fr. V. v. Hahn, cf. p. 416); further, in processes in which sulphide sols are formed (cf. p. 517).

What properties of the sulphides are connected with the fact that some give more stable, others less stable, colloidal solutions, has not yet been cleared up. The following circumstances will be of importance. In the first place, the solubility of the sulphides; the more difficultly soluble,

[1] *Freundlich* and *Nathansohn, loc. cit.* p. 488.
[2] *Freundlich* and *Schucht*, Zeitschr. f. physik. Chemie, **80**, 568 (1912).
[3] *Winssinger*, Bull. Acad. Roy. Belg (3), **15**, 390 (1888); *Freundlich* and *Schucht*, Zeitschr. f. physik. Chemie, **85**, 643 (1913).
[4] *E. A. Schneider*, Zeitschr. f. anorg. Chemie, **5**, 93 (1894).
[5] *Winssinger*, Bull. d. l. soc. chim. de France, **49**, 452 (1888).

the slower will be the growth to crystalline sulphide particles. Then it will depend how far the sulphide tends to be charged up by active electrolytes (H_2S, sulphides, and so on).

Winssinger [1] prepared a large number of sulphide sols; besides those already mentioned, the sols of Tl_2S_3, Bi_2S_3, Mo_2S_3, WS_3, FeS, CoS, NiS, PdS, PtS_2, and others. Sb_2S_3 sols are usually prepared according to directions by H. Schulze.[2]

Hydrosols of Difficultly Soluble Salts

Among difficultly soluble salts, the sols of which may be easily prepared, we may mention particularly some silver salts [3] (halides, phosphates, and others), and further some ferro- and ferri-cyanides.[4] Graham had already prepared colloidal solutions of Prussian blue, Turnbull's blue, and copper ferrocyanide. The method of preparation is entirely similar to that considered in the case of sulphide sols; solutions of the substances concerned in the reaction are allowed to interact in a suitably dilute form, the excess of electrolyte being removed by dialysis.

Lottermoser (cf. p. 372) was able to show exactly in the case of sols of difficultly soluble silver salts prepared in this way, that a certain residue of electrolyte must be present in order that the sol may be formed. Sols of Prussian blue and copper ferrocyanide act in a manner quite similar to that of these silver salts. The green colour of dilute Prussian blue sols in excess of alkaline ferrocyanide depends, as Bachmann [5] has shown, not upon the presence of a chemically different substance, but upon the extremely fine state of division of the Prussian blue, and upon the appearance of a mixed colour with the yellow of the colloidal iron hydroxide derived from the $FeCl_3$.

Another method of preparation depends upon dissolving the freshly precipitated, difficultly soluble compound in a suitable liquid and dialysing. Thus Prussian blue may be dissolved in an aqueous solution of oxalic acid or of an oxalate and purified by dialysis. Further, many sols may be obtained from others. If an amount of chlorine water, insufficient for complete reaction, be added to a silver sol, a colloidal solution of the photochloride is obtained—the colloidal mixture of silver and silver chloride which is contained in silver chloride which has been exposed to light (see details on p. 803).

Hydrosols of the Metallic Hydroxides, which are Allied to Hydrophobic Sols

Condensation methods are here most prominent. They often assume a particularly simple form, since the hydroxide frequently results from a hydrolysis, in which the dispersion medium, water, frequently takes part; it is sufficient to dialyse a solution of the corresponding metallic salt in suitable dilution in order to obtain the metallic hydroxide sol in question. If the resulting micellæ are positively charged, it is important to choose a metallic salt, the anion of which flocculates only weakly. W.

[1] *loc. cit.* p. 518.
[2] Journ. f. prakt. Chemie, **27,** 320 (1893).
[3] *Lottermoser* and *E. v. Meyer,* Journ. f. prakt. Chemie, **56,** 247 (1897); *Lottermoser ibid.* **57,** 484 (1898); **68,** 341 (1903); **72,** 39 (1905); **73,** 374 (1906).
[4] *Th. Graham,* Lieb. Ann. **121,** 48 *et seq.* (1862).
[5] Zeitschr. f. anorg. u. allg. Chemie, **100,** 77 (1917).

Biltz [1] prepared in this way the hydroxide sols of Al_2O_3, Fe_2O_3, Cr_2O_3, ZrO_2, CeO_2, ThO_2, by dialysing the corresponding nitrate solutions.

The hydrolysis may be increased by working in the warm. Thus, according to Krecke,[2] a Fe_2O_3 sol may be prepared by allowing a $FeCl_3$ solution to drop into hot water; Ufer [3] then dialysed this solution hot.

It is frequently advantageous to start from a concentrated salt solution, to peptize in this the hydroxide freshly precipitated with alkali, and then to dialyse the solution enriched in hydroxide. Upon this depends the usual method for obtaining Fe_2O_3 sols [4]; ammonium carbonate solution is added drop-wise to a $FeCl_3$ solution as long as the freshly precipitated flakes are peptized in the solution, which is then dialysed,

In many cases a freshly precipitated hydroxide may be brought into colloidal solution by washing out with water or with a solution of a peptizing electrolyte. Thus, another method for preparing a Fe_2O_3 sol depends upon precipitating a $FeCl_3$ solution with NH_3 solution and then peptizing the washed hydroxide with a dilute $FeCl_3$ solution.[5] In a similar manner, ZrO_2 and ThO_2 sols, among others, may be obtained by precipitating $Zr(NO_3)_4$ and $Th(NO_3)_4$ solutions with NH_3, washing, and peptizing with a dilute solution of the metallic nitrate.[6] In this method the behaviour discussed on p. 372, that a small excess of an electrolyte is necessary for the stability of a sol, appears very clearly.

Now it is not at all necessary, as Szilard [7] has shown, to peptize the hydroxides with a salt of the same metal: salts of other metals may also be taken, provided that they are sufficiently hydrolysed. Thus, he peptized ferric hydroxide with thorium acetate, thorium hydroxide with uranyl acetate, uranyl hydroxide with thorium acetate, and so obtained a great variety of sols. This phenomenon is frequently of importance in analytical chemistry. With mixtures of oxides and hydroxides, an oxide otherwise difficultly peptizable may be easily brought into colloidal solution by the presence of another, and a behaviour thus simulated which is not proper to the oxide in its pure state. Thus, according to O. Hahn and Gille,[8] pure tantalic acid is very slightly soluble in a mixture of H_2O_2 and H_2SO_4; on the other hand, it is very soluble, giving a colloidal solution, when titanium is present, Altogether, in analytical chemistry the fact that hydroxides usually separate colloidally must be repeatedly taken into account. Galecki [9] investigated the separation of iron and aluminium from manganese by the acetate method, and explained the best directions on a colloido-chemical basis. To this group of phenomena doubtless belongs the power of Cr_2O_3, peptized in alkali, of holding other hydroxides (iron, cobalt, nickel, and others) in colloidal solution.[10]

In many cases the manner in which the resulting precipitate, which is to be peptized to a hydroxide sol, undergoes, during washing, changes which

[1] Ber. d. deutsch. chem. Ges. **35,** 4434 (1902).
[2] Journ. f. prakt. Chemie (2) **3,** 286 (1871).
[3] "Ueber Kolloides Eisenoxyd," Diss., Dresden, 1915. There also an historical review of the most important work concerning Fe_2O_3 sols will be found.
[4] *Th. Graham,* Lieb. Ann. **121,** 45 (1862).
[5] E.g. *Maffia,* Kolloidchem. Beiheft, **3,** 93 to 94 (1912).
[6] *A. Müller,* Ber. d. deutsch. chem. Ges. **39,** 2859 (1906); Zeitschr. f. anorg. Chemie, **52,** 316 (1907).
[7] Journ. Chim. Phys. **5,** 488 and 636 (1907).
[8] Zeitschr. f. anorg. u. allg. Chemie, **112,** 283 (1920).
[9] Bull. de l'Acad. Scienc. d. Crac. 1913, p. 572.
[10] *C. F. Nagel,* Journ. Phys. Chem. **19,** 331 (1915).

make it suitable for peptization, is unmistakable. For Crum's [1] Al_2O_3 sol, already frequently referred to, one starts with a solution of aluminium acetate of about 8 per cent., of which 5 parts are mixed with 3 parts of concentrated acetic acid. Upon heating a basic salt separates, the "diacetyl aluminium hydroxide," in a crystalline form. This is washed with distilled water, whereby the originally crystalline precipitate passes more and more into a sticky mass of amorphous appearance, while the wash water, at first clear, becomes more and more turbid. This mass is peptized by energetic stirring with an excess of water and the liquid gently warmed until the odour of acetic acid has disappeared.

If the hydroxide to be peptized has an acid character, it must be liberated from the salt in a corresponding manner by means of an acid. The V_2O_5 sol frequently referred to is made by triturating solid NH_4VO_3 with HCl, washing the red flakes of separated V_2O_5 with water, upon a filter, until it commences to run through, and then peptizing the product by shaking with water.[2] Small amounts of NH_4VO_3 doubtless act as active electrolyte. To the group of these negative hydroxide sols belong further Mo_2O_5,[3] Nb_2O_5,[4] Ta_2O_5,[4] OsO_2,[5] and other sols.

Although hydrolytic reactions, and those in which the hydroxide is directly concerned, largely preponderate, cases are also known, in which the desired oxide is gained by reduction or oxidation. Thus MnO_2 sols are prepared by reducing a neutral permanganate solution with hydrogen peroxide,[6] or with a feebly alkaline solution of sodium arsenite [7]; in the latter case it is unnecessary to remove the arsenite by dialysis. Spring,[8] finally, prepared such sols by oxidizing $Mn(OH)_2$ with hypochlorous acid and peptizing the reaction product with water.

In the case of a series of electrolytic reactions which lead to oxide and hydroxide sols, it is likewise a matter of oxidation or reduction.

McCutcheon and E. F. Smith [9] prepared colloidal solutions of Al_2O_3, Y_2O_3, and other substances, by electrolysing dilute $AlCl_3$ and YCl_3 solutions with an amalgam cathode and rotating silver anode. In the electrolytic reduction of uranyl chloride solution Samsonow [10] obtained a black precipitate of UO_2, which could be directly peptized in water.

As repeatedly pointed out, many of these hydroxide sols are no longer true hydrophobic sols, but closely approach the hydrophilic sols in character. In contrast to the sols of the metals, sulphides, and so on, it is often in their case difficult to recognize single particles under the ultramicroscope. This does not depend alone upon the fact that the particles are smaller, but mainly upon the smaller difference between the refractive indices of micellæ and intermicellar liquid (cf. p. 387), and this again has

[1] Lieb. Ann. **89,** 156 (1854); see also *Gann, loc. cit.* p. 416.

[2] *W. Biltz,* Ber. d. deutsch. chem. Ges. **37,** 1098 (1904).

[3] *Freundlich* and *Leonhardt, loc. cit.* p. 451.

[4] *Hauser* and *Lewite,* Zeitschr. f. angew. Chemie, **25,** 100 (1912). They were prepared by fusing Nb_2O_5 and Ta_2O_5 with alkali in a silver crucible, and subsequently dialysing.

[5] *Ruff* and *Rathsburg,* Ber. d. deutsch. chem. Ges. **50,** 484 (1917).

[6] *Bredig* and *Marck, loc. cit.* p. 489.

[7] *Deiss,* Kolloidzeitschr. **6,** 69 (1910).

[8] Ber. d. deutsch. chem. Ges. **16,** 1143 (1883); see also *Witzemann,* Journ. Amer. Chem. Soc. **37,** 1079 (1915). There older literature concerning these sols will be found, which are among the oldest known.

[9] Journ. Amer. Chem. Soc. **29,** 1460 (1907).

[10] *loc. cit.* p. 390.

its cause in the far greater water content of the micellæ, on account of which they differ much less from the surrounding liquid. The higher water content has the further result that the properties of the dispersion medium are frequently more strongly altered than in the case of true hydrophobic sols, as soon as the content of disperse phase is large enough; the micellæ annex a considerable portion of the dispersion medium. This appears in particular in the fact that the viscosity of the sols of larger content is sensibly greater than that of water; the active volume φ is already considerable.

The fact that, in the case of hydroxide sols, one must take chemical changes in the micellæ into account to a greater degree is doubtless connected with the greater water content of the micellæ. The micellæ of a given gold sol may differ from those of another, prepared by a different method, in the nature of the active electrolyte, its amount, and so on. But the gold content forms so considerable a part of the micella that these differences are mainly of the second order. The same is true of other metallic sols, sulphide sols, and the like. With the hydroxide sols, on the other hand, the possibility is very great that we may be dealing with an hydroxide richer or poorer in water or even with a basic salt containing more or less water. In short, with sols prepared by different methods there is no guarantee that there may not be very fundamental chemical differences between the micellæ. There is much that points in this direction. The brown red Fe_2O_3 sols prepared in the cold differ sensibly in colour from the brick red sols prepared in the warm. If the brown red sol prepared in the cold is heated in a silver tube to 200°, it changes into a brick-red sol. A brick-red sol of this kind is also obtained by long boiling of a ferric acetate solution. These sols are frequently called sols of metaferric hydroxide. That the reactive power or reaction velocity of the micellæ has been changed thereby follows from the fact that upon passing H_2S the brown-red particles are changed to black sulphide, whilst the brick-red sols are not.[1] The sols obtained by dialysis alone apparently contain, in general, particles richer in water than those obtained by the peptization of precipitated flakes. For they are far clearer, the difference in refractive index between micellæ and intermicellar liquid is smaller than in the case of the cloudy opalescent sols, such as are frequently obtained by the peptization of flocculated hydroxides. This contrast is especially noticeable in the case of ZrO_2 and ThO_2 sols; this question will be dealt with later (cf. p. 633).

In the case of many hydroxide sols the transition to a true salt solution takes place continuously, easily, and reversibly. If one starts with a solution of a metallic salt, e.g. a $FeCl_3$ solution, containing, from the first, some hydroxide colloidally dissolved, and dialyses it, the relative colloid hydroxide content increases continuously, that of the Cl′ ion decreases, and simultaneously, the sensitiveness to flocculating electrolytes increases. If, on the other hand, increasing amounts of HCl are added to a Fe_2O_3 sol poor in Cl′ ions, the amount of hydroxide decreases, and the electrolyte content increases, until we again have a more or less hydrolysed salt solution.[2] That the content of colloidally dissolved hydroxide sensibly determines the behaviour of many solutions of salts

[1] *E. A. Schneider*, Ber. d. deutsch. chem. Ges. **24**, 2242 (1891).

[2] *J. Duclaux*, Kolloidzeitschr. **7**, 73 (1910); *Kuriloff*, Zeitschr. f. anorg. Chem. **79**, 88 (1913); *Neidle*, Journ. Amer. Chem. Soc. **39**, 2334 (1917).

of heavy metals, is well known ; thus the so-called ageing of these solutions arises from this cause.[1]

In spite of their relationship to hydrophilic sols, the hydroxide sols have nevertheless been dealt with in the foregoing section of lyophobic sols, since they correspond to these in their conditions of stability to so large an extent. They are, in fact, decidedly electrocratic ; in as pure a state as possible they are distinguished by a considerable kataphoretic migration velocity of definite sign, and by a sensitiveness to electrolytes in small concentrations, even to such as the alkali salts of inorganic acids. Basic hydroxides, such as those of iron, aluminium, chromium, and so on, give positive sols ; acid hydroxides, such as those of quinquevalent vanadium, niobium, tantalum, etc., negative.

The Hydrosols of Radio-active Substances

When solutions of radio-active substances were investigated, phenomena were encountered which hardly permitted of any other interpretation, than that these substances sometimes enter into colloidal solution. The following experiment by Paneth [2] is particularly striking. He dialysed a neutral solution of radio-lead nitrate against pure water ; the solution further contained, besides lead, RaD, RaE, and polonium. Lead and RaD dialysed straight through ; RaE and polonium, on the other hand, did not. This may be explained on the basis that RaD, like lead, with which it is isotopic, is crystalloidally dissolved as nitrate ; RaE, on the other hand, is isotopic with bismuth, its nitrate might be completely hydrolysed, and the hydroxide perhaps incapable, as a colloid, of passing through the membrane. Of polonium, which is a higher homologue of tellurium, we cannot say straight away in what form it may be present ; but that its nitrate is to a great degree hydrolysed and the hydroxide then remains colloidally dissolved, is not improbable. If the hydrolysis is depressed by addition of acid, RaE and polonium also pass through the membrane. In ammoniacal solution—a solution of polonium and thorium B (isotopic with lead) was investigated—the dialysis was still less than in neutral solution.

These experiments were completely confirmed by measurements of pure diffusion. Polonium and ThB had a much smaller diffusion coefficient in ammoniacal solution than in acid, in which the diffusion coefficient of the salt in question was found as theoretically calculated. Thus the diffusion constant of polonium, calculated in sq. cm./days, was 0·19 in $\frac{1}{2}$N NH_3 solution against 0·77 in acid. With ThB the corresponding figures were 0·37 and 0·68.

From quite another side Godlewski [3] arrived simultaneously at the view, that we often have to deal with colloidal solutions in the case of solutions of radio-active substances. He electrolysed such solutions and found that their unusual behaviour could not be explained upon the supposition of electrolytically migrating ions, while all observations could be easily correlated upon the assumption of a kataphoresis of colloid particles.

[1] See e.g. *Denham*, Zeitschr. f. anorg. Chem. **57**, 378 (1908).

[2] Sitzungsber. d. K. Akad. d. Wiss. zu Wien, **121**, 2193 (1912) ; Kolloidzeitschr. **13**, 1, 279 (1913).

[3] Bull. d. l'Acad. d. Scienc. d. Crac. 1913, 335 ; 1914, 30 ; Kolloidzeitschr. **14**, 229 (1914).

The phenomena in the case of radium emanation will now be considered. Let us take an aqueous solution of emanation. This decays in course of time, and the elements RaA, B and C, which have so short a life that their presence and amount can be readily determined from the curves of decay, are formed from it; and all three will be present together in water. All three elements have a metallic character; RaA is isotopic with polonium, RaB with lead, RaC with bismuth. If they were present in solution as ions, one would expect them to be deposited during electrolysis on the cathode in accordance with their position in the electrochemical series and with their concentration. This is, however, not at all the case; on the contrary, RaA is formed at the anode, RaB at the cathode, and RaC partly at anode and partly at cathode. This behaviour would be intelligible if we assumed we were dealing with a kataphoresis. The particles of RaA would be present as negative micellæ, which is entirely probable, whether we regard them as metallic or as oxide particles. It is equally probable that RaB gives a positive sol, since sols of lead oxide are positive. With RaC one might be in doubt, but a negative sol is, as a rule, more probable. That RaC appears partly at the anode and partly at the cathode might have the following cause. It is formed from RaB by a β-ray change. The force of the radio-active recoil is therefore small. If a RaC atom is formed in a group of RaB atoms, it will not necessarily get free of them, but will migrate with them in a colloidal mixture to the cathode, just as do, say, particles of a negative sol in an excess of positive particles (cf. p. 477). RaB, on the other hand, is sharply separated from RaA, since it arises from the latter by an α-ray change, and the force of recoil is great.

$H^{\cdot}$ and OH' ions, multivalent kations and anions, acted exactly as one would expect. Acids will charge positive particles more strongly, and will first flocculate and then reverse the charge of negative ones. In actual fact, the amount of RaB which separates at the cathode increases in acid solution; the amounts of RaA and RaC which separate at the anode decrease, and at higher concentrations of acid RaA and RaC likewise appear at the cathode (reversal of charge). At much larger $H^{\cdot}$ ion concentrations, in normal solution, the activity of the cathode greatly decreases. This points to the radio-active metals now being dissolved to ions and being deposited only in very small amounts in accordance with their excessively low concentration. In agreement with this is the fact that RaB, which dissolves most easily in acids, is the first to commence to decrease in amount.

The behaviour on addition of alkali is exactly the converse. The amount of RaB on the cathode first decreases, since it is flocculated, and at higher OH' ion concentrations it appears at the anode in consequence of the reversal of charge; the amounts of RaA and C increase at the anode.

The $Al^{\cdots}$ ion greatly decreases the amounts of the anodically deposited substances (coagulation), at somewhat greater concentrations it causes them to appear at the cathode (reversal of charge). The citrate ion forms again the counterpart.

The interaction between these sols of radio-active substances and other positive and negative sols obeys the theory discussed on p. 477. The phenomena in capillary analysis are somewhat ambiguous. In many cases the behaviour is according to theory; in others, no rise in the filter paper is observed when we should expect it. This may, however, be easily

explained by the small amounts of the radio-active element being adsorbed by the filter paper.

Surprisingly good as is the experimental confirmation of the consequences of this view, the fundamental difficulties raised by it are great. If we are dealing with metals, as in the case of derivatives of radium emanation just discussed, one can well imagine that even groups of only a few atoms, or indeed a single atom, can form a micella with a considerable number of water molecules. In the gas space as well, the atoms of these elements form large ions, of about $10\mu\mu$ diameter, containing numerous molecules.[1] But we then see that, as will be discussed on p. 532, we must certainly distinguish between molecular dispersity and true solution. We should have here a molecularly disperse solution of the radio-active metals, but this has by no means the character of a true solution, but rather that of a colloidal one, since obviously the interaction between dissolved substance and solvent, which is necessary to the formation of the proper solution molecule, does not take place.

If the particles are regarded as hydroxide particles, the difficulties are greater. The amounts in question are so small, that the hydroxides must be completely dissociated into their ions, and cannot be present as hydroxide micellæ. We may assume with Paneth that the solubility of ThB hydroxide is equal to that of lead hydroxide, viz. 5×10^{-4} mols per litre. If now dissociation occurs according to the equation

$$ThB(OH)_2 = ThB^{\cdot\cdot} + 2OH'$$

then the solubility product at complete dissociation would be

$$(ThB^{\cdot\cdot})(OH')^2 = 1{\cdot}25 \times 10^{-10}.$$

The concentration of the dissociated NH_4OH amounted in one experiment to 3×10^{-3}. The ThB concentration would have therefore to be about $1{\cdot}4 \times 10^{-5}$ molar, in order to reach the solubility product. It was in reality only of the order 10^{-11}, or about a million times smaller.

Zsigmondy[2] would like to explain the contradiction by the assumption that the micellæ do not simply consist of the hydroxides of the radio-elements, but of these hydroxides adsorbed on other colloidal hydroxide particles which are present in the water from the outset, and with which they move. This would require the radio-elements to be specifically adsorbed, in the sense of the element with the more difficultly soluble hydroxide being also more readily adsorbed by the water colloid in question than the one with the more easily soluble hydroxide. Now in actual fact there exists the relation considered on p. 220, that the radio-elements are the more strongly adsorbed by difficultly soluble adsorbents, the more difficultly soluble is the same compound of the radio-element under these conditions. We should therefore have every right to suppose that a more difficultly soluble RaC hydroxide is more freely adsorbed by colloidal Al_2O_3 particles present in the water as impurity, than a more easily soluble RaB hydroxide. It is true that we must make the further assumption, that both positive and negative colloid particles are present in water as impurities, and that these do not mutually destroy one another, perhaps because their amounts are so small.

[1] *Debierne*, Le Radium, **6**, 97 (1909); *Eckmann*, Jahrb. d. Radioaktiv. u. Elektr. **9**, 195 (1913).

[2] cf. *Paneth*, Kolloidzeitschr. **13**, 304 (1913).

Hydrophobic Sols of Organic Substances

Many organic substances give emulsions and suspensions or colloidal solutions in water, which have a completely hydrophobic character. The oil emulsions investigated by Ellis [1] and Powis [2] have frequently been referred to. They were prepared by shaking a cylinder oil, as acid-free as possible (it contained about 0·3 per cent. acid), a petroleum hydrocarbon therefore, with pure water for several days. The mastic suspension is a further example. It behaves exactly like a hydrophobic sol, even as regards flocculation by electrolytes (cf. p. 428). These suspensions are made by pouring an alcoholic mastic solution into an excess of water. With correct dilution and in presence of suitable peptizing electrolytes this method is of very general applicability, and allows of the preparation of sols of many organic substances, such as anthracene, p-azoxyanisole, cholesterol,[3] and others. The colloidal solutions of lecithin, on the other hand, like Odén's sulphur sols, stand to such an extent upon the boundary between hydrophobic and hydrophilic sols, that it is better to deal with them later (p. 647). The same is true of solutions of dyes, although many of them, such as those of Congorubin, benzopurpurin, aniline blue, are so hydrophobic [4] that they could unhesitatingly be regarded as examples of hydrophobic sols.[5]

It may further be pointed out, that the colloidal saponarin solutions investigated by Barger,[6] which are coloured blue by iodine, are flocculated by electrolytes entirely according to the rules which hold for negative hydrophobic sols. Among hydrophilic sols we meet with many further cases, in which a hydrophilic sol may be converted into a hydrophobic one by suitable methods (cf. p. 607).

Non-aqueous Lyophobic Sols

Lyophobic Sols in Organic Dispersion Media

Sols in organic dispersion media have been prepared in considerable numbers, with considerable variation in dispersion medium and disperse phase. Sols are known in hydrocarbons, such as methane and pentane, in alcohols (methyl, ethyl, isobutyl alcohol, and others), in glycerine, in ethyl ether, and others. As disperse phase we meet especially with metals and elements such as selenium and tellurium, and only rarely with sulphides and salts. Hardly anything trustworthy is known however, concerning the conditions of stability, so that at the present it is more or less arbitrary whether one describes the sols as lyophobic or lyophilic. By analogy with the behaviour in water, those will be regarded as lyophobic in which the micellæ strongly contrast in nature with the intermicellar liquid.

Best known are the sols of the metals, since in their case especially the Svedberg [7] method of disintegration by oscillatory discharge may be applied.

[1] *Loc. cit.* p. 418. [2] *loc. cit.* p. 418.

[3] *Porges* and *Neubauer*, Biochem. Zeitschr. **7**, 152 (1908); *Berczeller*, Biochem. Zeitschr. **66**, 218 (1914). The carefully purified cholesterol produces no depression in the surface tension, but impure preparations frequently do so; see also *Wedekind*, Kolloidzeitschr. **8**, 303 (1911).

[4] Also the sol of paranitraniline red described by *Haller* [Kolloidzeitschr. **22**, 117 (1918)] is hydrophobic.

[5] The solution of pentamercuric-acetanilide acetate described by *Raffo* and *Rossi* [Kolloidzeitschr. **11**, 120 (1912)] has a more hydrophilic character.

[6] *loc. cit.* p. 189. [7] *loc. cit.* p. 509.

It has already been mentioned above that Svedberg succeeded in this way, at the temperature of liquid air and in a hydrogen atmosphere, in preparing sols of lithium, sodium, potassium, rubidium, and cæsium in methane, pentane, and ethyl ether. The distinctive behaviour of the colour of these sols has already been discussed on p. 385. In ethyl ether and isobutyl alcohol as dispersion media he also peptized many other metals, noble ones such as silver, gold, and the platinum metals, and also light and heavy metals (Ca, Sr, Ba, Zn, Cd, Hg, Al, La, Ce, Tl, Sn, Pb, As, Sb, Bi, V, Ta, Cr, Mo, W, U, Mn, Fe, Co, Ni).

Although the details of the conditions of stability of these sols are not clear, the general view agrees completely with the behaviour as observed with water as dispersion medium. While water as a strongly dissociating dispersion medium represents the one limiting case, ethyl ether may be taken as the opposite example of a weakly dissociating dispersion medium. It then appears in the first place, that the power to dissociate and hence to charge electrically is so necessary for the preparation of colloidal solutions, that at ordinary temperature with fairly pure ethyl ether a metallic sol cannot be prepared. Two ways are known of overcoming the difficulty; in the first place one can add to the ethyl ether substances which favour colloid formation. These are substances which increase the dissociating power of the dispersion medium and hence favour the formation of carriers of electricity; for water, benzoic acid, and other substances are of this class. If about 4 per cent. of water is added to ethyl ether, a platinum sol can be prepared at room temperature.

Then, the stability depends very greatly upon the temperature, really more strikingly, than has, as a rule, hitherto been observed in the case of hydrosols. The temperature coefficient is so great, that we may straightway speak with Svedberg of a *critical temperature of flocculation*, above which a sol is unstable, while below it it can be kept for a longer or shorter period of time. It was shown ultramicroscopically, in the case of a platinum sol in ethyl ether, that at the critical temperature of flocculation the number of particles apparently decreases greatly quite suddenly.[1] It has already been frequently pointed out, that one must necessarily be able to determine a critical value of a certain parameter, if the differential coefficient of the property in question with respect to this parameter is large enough; thus a "metastable limit" can be found for the velocity of formation of nuclei, a threshold value for the velocity of coagulation. Matters are no doubt similar in this case.

That a metal sol cannot be successfully prepared at room temperature with ethyl ether depends upon the fact that with all metals hitherto investigated the room temperature is above the critical temperature of flocculation. If we cool sufficiently—in which case we must cool more strongly the purer the ether—a sol can be successfully prepared. Table 139 shows the connexion between water content of the ether and critical temperature of flocculation $\mathbf{t}_k$; the temperature $\mathbf{t}_z$ is also given, which was that of the dispersion medium during disintegration.

We may assume that small impurities are still responsible for the stability of sols which can only be kept at very low temperatures; for Svedberg succeeded in purifying ether so carefully that a platinum sol was unstable even at $-80°$.

With other substances, such as benzoic acid, a maximum of stability

[1] *Svedberg* and *Inouye*, Kolloidzeitschr. **9**, 153 (1911).

TABLE 139

Critical Temperature of Flocculation of a Platinum Ethyl-ether Sol containing Water

Water Content in grams per litre of Solution.	t_k in degrees.	t_z in degrees.
Traces	− 48	− 78
,,	− 28	− 74
,,	− 8·5	− 20
,,	− 6·7	− 20
1·50	− 0·8	− 20
3·01	+ 11·5	− 20
3·87	+ 21·0	+ 15
3·87	+ 23·0	+ 15
3·87	+ 22·2	+ 15
7·74	+ 39	+ 15
38·7	Stable on boiling	+ 14
77·4	,, ,, ,,	+ 14

appears with increasing concentration; the foreign substance acts not only as peptizing agent, but also as coagulator.

What property actually determines the large temperature coefficient of the velocity of flocculation, whether mainly only the formation of carriers of electricity or the great dependence upon temperature of the viscosity of the dispersion medium, cannot be stated. In the coarsening of colloidal particles and the concomitant reversal of adsorption a large temperature coefficient was also observed (cf. p. 467); whether this is more than an external similarity, is an open question. The stability of the sols also declines with increase in content of disperse phase.

Similar regularities hold for other noble metals in ether as in the case of platinum. The base metals give unstable sols and no sharply distinguished temperature of flocculation.

The sols in dispersion media the properties of which lie between those of water and ethyl ether, show conditions of stability which at present cannot be disentangled. The properties of the dispersion medium and of the disperse phase, and above all of the impurities, are of influence. In order to give an example of the manifold character of these relations we may mention that according to Svedberg [1] a platinum ethyl alcohol sol is unstable at room temperature, a platinum n-propyl alcohol sol stable; it does not even precipitate after heating for hours at 125°. Cerium, but not lanthanum, gives a stable isobutyl alcohol sol, platinum and palladium also give stable isobutyl alcohol sols, but not iridium. According to E. A. Schneider,[2] who worked with a silver alcohol sol prepared in quite another way (see p. 529), the latter was quickly flocculated by isopropyl alcohol, but not by propyl alcohol.

That the properties alter so greatly with small additions, reminds one of the conductivity of these dispersion media,[3] and points to the importance of the presence of carriers of electricity.

Burton [4] disintegrated a number of metals in some organic liquids

[1] Nov. Act. reg. soc. scient. Upsala (4), **2**, No. 1, p. 109.
[2] Zeitschr. f. anorg. Chemie, **7**, 339 (1894).
[3] cf. *Walden*, Zeitschr. f. physik. Chemie, **54**, 129 (1906).
[4] Phil. Mag. (6) **11**, 441 (1906).

according to Bredig's method. In methyl and ethyl alcohols this was only successful with base metals such as Zn, Sn, Pb, Bi, Fe; the noblest metal with which it succeeded was Cu. The particles of all these sols were positively charged. Conversely in ethyl malonate only noble metals (Ag, Au, Pt) could be dispersed. The sols were all negative. This led Burton to the following view. The alcohols act as weak bases and cause the peptized metals, coated with layers of oxide, to give positive hydroxide sols. Ethyl malonate, on the other hand, in accordance with its more acid nature, only gives up hydrogen. The noble metals hence form hydrides and are negatively charged. For the same reason they are also negatively charged in water. This argument would be more forcible if we were acquainted with dispersion media, in which the noble metals could be peptized to positive sols because hydride formation was excluded.

The Svedberg method is not the only one by which metallic sols may be prepared. E. A. Schneider[1] had previously prepared them in non-aqueous dispersion media, such as ethyl alcohol and glycerine, by dialysing aqueous metallic sols against repeatedly renewed quantities of the other dispersion medium. This method is obviously only applicable to liquids in which water is soluble, and which penetrate the diffusion membrane in presence of water, particularly, therefore, to liquids such as methyl and ethyl alcohol, for which also it was employed by Schneider. He obtained by this method not merely metallic sols such as those of silver in alcohol and glycerine, but also, for example, an alcosol of Au_2S_2. Silver sols were also prepared by peptizing in alcohol the washed flocculation product of a Carey Lea silver sol.

Wa. Ostwald[2] prepared colloidal solutions of nickel in benzene, by decomposing a solution of $Ni(CO)_4$ in this liquid by warming.[3] Pyridine is a dispersion medium in which sols may easily be prepared. With a number of metals (Ag, Ni and others) Pieroni and Girardi[4] have prepared colloidal solutions by reducing solutions of the metal in question with pyrogallol. Sulphur sols were obtained by decomposing solutions of sulphur or of potassium polysulphide in pyridine with water. By illuminating solutions of rhombic sulphur in benzene, tetrachloromethane and chloroform, colloidal solutions of $S\mu$ sulphur are obtained.[5] Phosphorus also separates at first in colloidal form when its solution in CS_2 is illuminated.[6] Here we may also consider the solutions of iodine in water and in many organic solvents. An ultramicroscopic investigation of Amann[7] proved that in many cases micellæ may be recognized, which frequently only appear on illumination, or are altered thereby in a characteristic manner. We must distinguish alongside truly dissolved particles—iodine ions, iodine molecules, molecules consisting of iodine and the solvent—further a large series of micellæ. Such colloidal solutions should no doubt more correctly be included amongst the hydrophilic sols.

Sols of salts, etc., can also be obtained by allowing the condensation

[1] Ber. d. deutsch. chem. Ges. **25**, 1164 (1895).

[2] Kolloidzeitschr. **15**, 204 (1914).

[3] The nickel sols used in the hydrogenation of oils are prepared by reduction at a gentle heat of organic nickel salts. See *Ellis*, "Hydrogenation of Oils," London, 1919. [*Trans.*]

[4] Kolloidzeitschr. **15**, 159 (1914).

[5] *Wigand*, Zeitschr. f. physik. Chemie, **77**, 423 (1911); *W. Biltz*, Kolloidzeitschr. **12**, 296 (1913).

[6] *Siedentopf*, Ber. d. deutsch. chem. Ges. **43**, 692 (1910).

[7] Kolloidzeitschr. **6**, 235 (1910); **7**, 67 (1910); Kolloidchem. Beiheft. **3**, 337 (1912).

reaction which takes place in water, to take place in the dispersion medium in question. Suitable peptizing agents, and as low a temperature as the conditions of stability in the liquid in question generally require, must be provided for.

It happens sometimes, that the micellæ of a sol in water distribute themselves between the two phases upon shaking with an organic liquid; but the second phase must not be too different from the aqueous one; one must be in the neighbourhood of the critical point of mixture.[1]

(*b*) The Lyophilic Sols

It has been repeatedly emphasized that no fundamental difference exists between lyophobic and lyophilic sols, and that many intermediate steps between them are known. Nevertheless it appears advantageous to deal with the lyophilic sols in a special section. One would otherwise have been compelled to describe at the end of almost every paragraph of the foregoing section a behaviour for the pronounced lyophilic sols which was quite different from that described for the pronounced lyophobic ones. This appeared to me to be more disadvantageous than a certain lack of consistency lying in the fact that much that will now be said concerning lyophilic sols must to a certain extent be extended backwards over the lyophobic sols.

This section of colloid chemistry is particularly important. Structures so important for living processes as solutions of the proteins, of starch, and similar substances, fall under this heading. The more keenly therefore do we feel the defects of our knowledge of this part of the subject. Two circumstances render advance very difficult. In the first place we have the difficulties which lie in the methods of investigation. Many methods excellently applicable to lyophobic sols fail with lyophilic. Often very little can be done with the ultramicroscope, either because the micellæ are too small, or because the difference between the refractive indices of micella and intermicellar liquid is not great enough; so that a direct determination of the number and size of the particles cannot be effected. The electrokinetic behaviour is more complicated, since the particles of the lyophilic sols do not usually carry a charge of definite sign at the outset, but lie near to the isoelectric point, so that they easily change sign with small changes in the composition of the solution. It is therefore more difficult to draw any further conclusions from the electrical behaviour.

Still greater difficulties lie in the properties of the disperse phase itself of lyophilic sols. Colloidally dissolved substances such as proteins, carbohydrates, etc., are altogether disproportionately more reactive than the colloidally dissolved substances in most lyophobic sols. They tend above all towards reactions with the dispersion medium; in aqueous sols therefore to every possible hydrolytic reaction. This not merely directly renders all work more difficult, since it is never certain whether, after a shorter or

[1] *Lash Miller* and *McPherson, loc. cit.* p. 483.

The method by which graphite is peptized to form the colloidal suspension in oil due to Acheson and known as "oil-dag" is as follows. The graphite is kneaded long and thoroughly with water containing tannic acid to form a dough or paste; it then passes into the oil upon mixing with the latter. See Mem. on Solid Lubricants, Research Department, H.M. Stationery Office, London, 1920; *Dunstan*, III B.A. Rep. on Coll. Ch., p. 91. There has also been some question of using coal finely ground and suspended in oil as fuel. See *Dunstan, loc. cit.* above, and *Bates* and *O'Neill*, Inst. Petr. Techn., Nov. 16, 1920. [*Trans.*]

longer time, we are dealing with the same sol as at the start; it also renders it more difficult to draw any conclusion from the number and size of the particles. If, by means of any method, we find smaller particles, we do not know whether they are identical with the original particles, or whether they are chemically entirely different. To this is added the fact that these hydrolytic reactions are greatly dependent upon the $H^{\cdot}$ and OH' ion concentrations of the solution, and that these may change in consequence of these very hydrolytic reactions. Strictly speaking one should always attend to the invariability of the $H^{\cdot}$ and OH' ion concentrations in following the behaviour of hydrophilic sols.

Since these difficulties are very far from having been overcome, comparatively little can be said in general terms concerning hydrophilic sols. Hence the General Part is of smaller importance than the Special Part.

1. GENERAL PART

The Preparation of Lyophilic Sols and the Nature of their Micellæ

The lyophobic sols are largely artificial products prepared by special methods in the laboratory. The lyophilic sols, on the other hand, are often natural products, such as for example the many solutions of proteins occurring in the protoplasm or the body fluids of living beings; or they may be prepared more or less easily from naturally occurring solid substances by peptizing them in water or another dispersion medium. To this extent the preparation of a colloidal solution of starch, agar, gelatine, albumin and so on does not differ externally from that of a solution of a truly dissolved substance.

There are of course lyophilic sols which are prepared by methods similar to those used for lyophobic sols. Thus, the lyophilic sols of silicic acid and stannic acid may be prepared by acidifying the salts of silicic or stannic acids and dialysing them.

The similarity in the method of preparation alone causes the lyophilic sols to appear more similar than the lyophobic to ordinary solutions. They frequently differ from them externally by being slightly turbid, and showing therefore a distinct Tyndall cone, by not diffusing through membranes or doing so only very slowly, by producing a slight or no rise in the boiling-point of the dispersion medium, and by similarly lowering the freezing-point only slightly or not at all. The differences are therefore only of degree. Hence nothing stands in the way of the view that in lyophilic sols, as in true solutions, substances are divided down to their molecules, only that the molecules are so large that they produce the Tyndall effect, do not diffuse through membranes, and only produce a slight depression of the freezing-point and rise in boiling-point, because the molar concentration of the solution remains comparatively small. Without doubt we shall not be dealing in the case of the solution molecules with molecules of the solid substance in question, but these will have bound many molecules of water, so that amicronic or submicronic particles of the substance [1] which has undergone

[1] The German word "quellen," which means to take up water or other liquid, has no English equivalent. The verb "imbibe" and the substantive "imbibition" have been introduced into colloid chemistry, but "imbibe" is transitive, and the intransitive verb is still missing. "Swell" is often used and we say that gelatine swells up in water, but in the German scientific use of the word does not carry with it an increase in size; thus Freundlich speaks of surface of glass as "gequollen." Circumlocution can be used until we come to "quellbar," "able to imbibe water or other liquid." Here "imbibulous," in analogy with "bibulous" used of paper and the like, may lose its rather alarming aspect if it comes into use. [*Trans.*]

imbibition constitute the micellæ of the lyophilic sol. We rarely have at present the possibility of deciding whether these water molecules really assemble around the single molecules of the particular substance, or whether two or more molecules of the substance are contained in the micellæ in addition to the molecules of the dispersion medium.

Since it is possible, and indeed in many cases probable, that solutions of substances of high molecular weight, in which division has proceeded as far as the single molecules, possess the properties of colloidal solutions, it appears to me to be a good reason for only applying the conception "molecularly disperse" with caution; at any rate always with the consciousness that a continuous transition exists, and that a molecularly disperse solution may also assume the properties of a colloidally disperse solution. Further, in the case of the conception of molecular dispersity it must always be borne in mind that this does not include the chief characteristic of the true solution. It is less distinctive of the latter that the division of the solute has proceeded down to the molecules, than that comparatively small solution molecules which have been formed by the reaction of the solute with the solvent are present in it.[1]

Now this does not mean that lyophilic substances dissolved colloidally in this way are *non-electrolytes*; they may also be *electrolytes*, in which one ion is so large that it has the properties of a micella. As prototype of such a *colloid electrolyte solution* we must regard soap solutions, and then also many solutions of dyes, proteins, etc. In these the fact holds strongly that acids or bases are generally more weakly dissociated than salts. Hence the sols of the less dissociated acids or bases behave more like lyophilic sols of non-electrolytes.

In the case of hydrophilic sols, solutions also forming an unmistakable transition to true solutions are especially frequent and important; to these belong again soap solutions, and then the numerous dyes, the dextrins, etc. They dialyse perceptibly, although slowly, show a measurable depression of the freezing-point, but give viscous solutions, crystallize badly, dry to horn-like masses, and so on. It is frequently useful to term them *semi-colloids* or *half colloids*.

The kind of lyophilic sols frequently referred to above, in which the molecules of a substance, regarded as chemically homogeneous, "dissolve" in dispersion media with formation of such large solution molecules that they show the properties of micellæ, is the simplest case we can imagine. How far it actually occurs will not always be easy to decide. We shall indeed always have to take into account the possibility that peptizing agents may be present, that therefore the substances going into colloidal solution are not homogeneous, but that one substance, perhaps present only in small amount, peptizes the other; not to speak of other possibilities.

Density and Refraction of Lyophilic Sols

As regards density and refractive index, lyophilic sols are frequently not fundamentally different from lyophobic. Usually both properties are found to be linearly dependent upon the disperse phase content.[2] In

[1] See *Kruyt*, Kolloidzeitschr. **20**, 239 (1917).

[2] See particularly *Wintgen*, *loc. cit.* p. 365. There will be found measurements on the sols of silicic acid and tannin, and the discussion of earlier investigations by *Quincke* [Ann. d. Physik (4), **9**, 800 (1902), silicic acid; **10**, 509 (1903), tannin; **10**, 486 (1903), glue], *J. Frank* [Kolloidchem. Beiheft. **4**, 202 (1912), starch, gelatine],

other cases, especially where it has been possible to investigate also concentrated solutions (calculated molarly), as in the case of the soaps,[1] the dependence is complicated in a manner similar to that known for true solutions. The fact takes effect, that complicated equilibria, changing greatly with the concentration, exist between dispersion medium and disperse phase.

The Surface Tension and Related Properties of Lyophilic Sols

In the surface tension a clear distinction between lyophilic and lyophobic sols becomes evident. It is true that there are lyophilic sols, such as those of silicic [2] and stannic acids,[3] of starch,[4] and related substances, the surface tension of which, like that of hydrophobic sols, differs not at all or only very slightly from that of water. But others are sensibly or strongly surface active; thus proteins,[5] gum,[6] and other substances lower the surface tension of water fairly strongly, others, such as soaps,[7] saponins,[8] etc., very strongly. Previous statements on this subject must however only be employed with caution. For we know that minute amounts of surface-active substances suffice greatly to depress the surface tension, and the hydrophilic sols in question have rarely been so carefully purified that one may be sure that the observed depression really arises from the micellæ themselves and not from chance impurities. As an example we have the fact that especially purified casein only slightly lowers the surface tension of water, while the casein of commerce does so very distinctly.[9]

With substances giving such strongly surface-active sols as the soaps, there can naturally be no doubt that they themselves, or at least substances taking part directly in the equilibrium set up in these solutions, are the cause. The σ, c curves of soap solutions have throughout the character otherwise known with strongly surface-active solutions (cf. p. 61). Even at low concentrations σ is considerably lowered, then it remains practically constant at this small value over a large range of increase in concentration. The bend in the curve is often strikingly sharp with soap solutions.

The lowering of the surface tension has the result, that the colloidally dissolved substance collects at the surface in accordance with the Gibbs adsorption equation. This phenomenon takes much greater effect with hydrophilic sols than with true solutions. In the latter case special devices were necessary, and many difficulties had to be overcome before the transition from dynamic to static surface tension, and the collection of dissolved substances in the surface could be successfully demonstrated (cf. p. 51).

Herlitzka [Kolloidzeitschr. **7**, 250 (1910), protein], Miss *Chick* and *C. J. Martin* [Kolloidzeitschr. **12**, 71 (1913), various proteins], *Brailsford Robertson* [Journ. Phys. Chem. **13**, 469 (1909), Journ. Biol. Chem. **7**, 359 (1910), **8**, 287, 441, 507 (1910), coefficient of refraction of protein solutions], and others.

[1] Frl. *Cornish*, Zeitsch. f. physik. Chemie, **76**, 210 (1911).

[2] *Quincke*, Ann. d. Physik (4), **9**, 800 (1902).

[3] *Heinz*, "Ueber Kolloide Zinnsäuren wechselnden Alkaligehalts." Diss., Göttingen, 1914, p. 42.

[4] *Zlobicki*, *loc. cit.*, p. 366.

[5] *Quincke*, Wied. Ann. **35**, 582–583 (1888); *Bottazzi*, Rend. R. Accad. d. Linc. (5) **21**, II, 221 (1912); *Bottazzi* and *d'Agostino*, *ibid.* (5), **21**, II, 561 (1912).

[6] *Quincke*, *loc. cit.* under [5].

[7] *Rayleigh*, Proc. Roy. Soc. **47**, 281 (1890); *Bottazzi* and *Victorow*, Rend. R. Accad. d. Linc. (5), **19**, I, 659 (1910); *Bottazzi*, *ibid.* **21**, II, 365 (1912).

[8] *Rayleigh*, *loc. cit.* under [7].

[9] *Berczeller*, Biochem. Zeitschr. **53**, 232 (1913).

With hydrophilic sols, on the other hand, phenomena connected with this adsorption positively force themselves upon our observation. In the first place the difference between static and dynamic surface tension makes itself strongly felt; if one measures on a fresh surface, one gets a far higher value than after waiting for some time until equilibrium has been attained. Dupré [1] already mentioned this fact for soap solutions, when measuring σ on the one hand by the method of capillary rise, and on the other by a jet method (not dealt with further in the section pp. 12 to 23). We owe to Rayleigh [2] the first quantitative measurements on aqueous soap and saponin solutions (Table 140); the capillary rise again served as static method, and as dynamic that of oscillating jets (cf. p. 12) was used. In Table 141 some experiments of Berczeller [3] on sodium oleate solutions are also given in which the drop-numbers were measured with the stalagmometer, and in which the velocity with which the drops were formed was varied; one can thus form an idea of the time within which the static tension is set up. Reciprocal values of the drop numbers, which are proportional to the surface tension, are given, since in the case of sodium oleate solution it is not certain whether the static value of the surface tension is reached. In the table τ stands for the time necessary for the formation of a drop.

TABLE 140

Dynamic and Static Surface Tension of Hydrophilic Sols

Room temperature

Liquid investigated.	σ (dynamic).	σ (static).
Water	73	73
Sod. oleate solution (0·025 per cent.)	77	53
„ „ 0·25 „	77	25
„ „ 1·25 „	60	25
„ „ 2·5 „	56	25
Saponin solution	71	51

TABLE 141

Dependence of the Drop Number of a Hydrophilic Sol upon the Rate of Dropping

Liquid investigated.	τ (in secs.).	Drop Number.	Reciprocal Value of Drop Number.
Water	1·01	43·8	0·0228
„	2·92	43·8	0·0228
„	9·93	44·0	0·0227
„	16·0	44·0	0·0227
Na oleate (0·1 per cent.)	0·71	61·6	0·0163
„ „	2·08	72·2	0·0139
„ „	3·65	82·1	0·0122

[1] Ann. de chim. et de phys. (4), **7**, 409 (1866); **9**, 379 (1866).
[2] Proc. Roy. Soc. **47**, 281 (1890).
[3] Internat. Zeitschr. f. physik. chem. Biologie, **1**, 124 (1914).

Berczeller showed the existence of this phenomenon for a series of hydrophilic sols (of hæmoglobin, serum and egg albumin, casein, Witte's peptone, gelatine, saponin).

This also follows very clearly from experiments performed by Hiss in the manner discussed earlier (p. 51). While in the experiment given in Table 12, p. 53, with an aqueous solution of amyl alcohol only 0·015 sec. was required for the dynamic surface tension to decrease by 30 per cent., the same decrease with an old soap solution containing glycerine, with about 0·5 gram sodium oleate per litre, required about 0·11 sec.

The very pronounced character of this phenomenon depends in the first place upon these hydrophilic sols having a comparatively small molar concentration. Since a considerable quantity of the micellæ strives to reach the surface, the layers directly adjacent to the surface do not suffice to saturate the latter; more distant layers must assist. But since the velocity of diffusion of these micellæ is much smaller than that of truly dissolved substances, the time required to reach static equilibrium is considerably longer. The fact that, according to Berczeller, saturated aqueous solutions of camphor and thymol also require fairly long times for the development of the static tension is likewise no doubt due to the low concentration and to the great enrichment at the surface requiring diffusion from more distant layers.

Adsorption also comes into play in the separation of a film of the disperse phase on the surface of many hydrophilic sols, such as the proteins, soaps, many dyes, etc., even under conditions which exclude evaporation of the liquid. It is here scarcely a matter of a pure adsorption. For the films frequently have properties other than those originally possessed by the disperse phase. In the case of proteins, for example, they cannot be directly re-peptized by water; the protein is denatured (see p. 611). But one may suppose, that the first stage of the process is adsorption; upon this follows coagulation of the micellæ which are thickly packed on the surface, and thereupon a chemical change, which probably consists in a dehydration and molecular rearrangement. Ramsden,[1] who has investigated this phenomenon more closely, was able to show that one can completely free an albumin sol from albumin by shaking it and removing the foam, which contains a great deal of albumin. With mixtures of hydrophilic sols he observed that the more strongly capillary-active substance goes preferentially to the surface; in a sol containing albumin and saponin, the disperse phase which collected in the foam consisted almost entirely of saponin, which certainly lowers the σ of water more than albumin. The velocity with which solid films are formed on surfaces has also been measured. Since however it possibly depends chiefly upon the velocity of a coagulation, these processes will be discussed later (p. 750).

It is, in principle, immaterial whether the solid films are allowed to form by adsorption from the original uniform sol, or whether they are formed by allowing drops of the sol to spread out upon pure water. Devaux [2] and Metcalf [3] in particular have prepared films according to the latter

[1] Arch. f. Anat. und Physiol., Physiol. Abt. 1894, p. 517; Zeitschr. f. physik. Chemie, **47**, 336 (1904). The phenomenon was already explained by *W. Ostwald* [Zeitschr. f. physik. Chemie, **15**, 704 (1894)] on the basis of the *Gibbs* adsorption equation.

[2] Journ. d. Phys. (4), **3**, 450 (1904).

[3] Zeitschr. f. physik. Chemie, **52**, 1 (1905); there the older literature will also be found.

method. Metcalf worked with solutions of peptone; these give very firm films which undoubtedly consist of a reaction product of the peptone. Since in the spreading experiments the peptone is present at the outset on the surface in larger amount than corresponds to adsorption equilibrium, it diffuses in part into the interior of the liquid. Along with this occurs a hardening of the peptone film. The processes overlap, and since they are opposed, it is intelligible why in the time-course of the hardening the firmness of the film passes through a minimum.

Changes in a sol, coagulation of the micellæ, etc., are frequently reflected in changes in the surface tension, so that they may be followed with its aid.

The behaviour of lyophilic sols with respect to the *interfacial tension* between two liquids is entirely similar. How strongly the capillary activity of soap solutions appears in this connexion has already been touched upon earlier (p. 89). In Table 142 the depression of some interfacial tensions by a $\frac{1}{10}$ molar sodium oleate solution are given.

TABLE 142

Influence of Na Oleate upon the σ_{fl} of various Interfaces [1]

$t = 22°$

Interface against	σ_{fl} with Water as second Phase.	σ_{fl} with 0·1 molar aqueous Na oleate Solution as second Phase.
Air	72·4	30·4
Ethyl ether	10·4	1·71
Chloroform	29·4	2·09
Carbon tetrachloride	43·4	1·64
Nitrobenzene	25·5	2·54

Upon the lowering of the interfacial tension by soap solutions depends the fact that substances difficultly wetted with water, such as indigo, etc., can be made wettable by an addition of soapy water.

The adsorption of the particles of lyophilic sols by adsorbents such as charcoal, kaolin, etc., has a much greater resemblance to the adsorption of truly dissolved substances than has that of the particles of lyophobic sols (cf. p. 481). As in the case of adsorption in solution, the ordinary adsorption isothermal holds in small concentrations, the adsorption exponent has the value generally found, and with increase in concentration a saturation is reached. The saturation may also be exceeded, so that the adsorption isothermal shows a maximum. Examples of this adsorption of the micellæ of hydrophilic sols, such as solutions of dextrin, gum, etc., by adsorbents such as $CaCO_3$, $SrCO_3$, etc., have already been mentioned (p. 219). To determine the content of the colloidal solution, the liquid interferometer of F. Löwe has frequently proved of value.[2] As further examples, the adsorption of egg-albumin by ferric oxide and by cellulose

[1] According to measurements by *Lóránt, loc. cit.* p. 87.

[2] *F. Löwe*, Kolloidzeitschr. **11**, 226 (1912); *R. Marc*, Chemikerztg. **36**, 537 (1912); Kolloidzeitschr. **11**, 195 (1912).

(W. Biltz [1]), of euglobulin and other proteins by silicic acid, meerschaum, kaolin, etc. (Landsteiner and Uhlirz [2]), and of tannin and dextrin by fibrous alumina (Wislicenus [3]) may be mentioned. In the adsorption of dextrins by ferric oxide gel, which obeys the ordinary adsorption isothermal, W. Biltz [4] found an unmistakable symbasis with the molecular weight of the dextrins, as determined from the osmotic pressure (see p. 557). An amylodextrin with a molecular weight of about 20,000 was adsorbed by far the most strongly, an achroodextrin with one of 10,000 less strongly, and dextrins with molecular weights from 3,000 to 5,000 were adsorbed least of all. The same phenomenon often appears in the adsorption of the micellæ of hydrophilic sols as in adsorption upon a surface in contact with gas (cf. p. 535), namely, that it is not smoothly reversible ; thus for instance with Biltz's [5] experiments on egg-albumin. Probably we have here the same process of denaturing as in the case of adsorption at a surface. It is perfectly intelligible that the hydrophilic sols follow true solutions so closely in their behaviour with regard to adsorption. The pure electrical properties which, in the case of hydrophobic sols, so strongly influence the taking up of colloid particles by adsorption (cf. p. 480), fall very much into the background with hydrophilic sols.

One will have no doubt that the micellæ of a hydrophilic sol can also act as adsorbent and adsorb truly dissolved molecules. A really carefully investigated example of this is scarcely known ; the micellæ of a sol which have adsorbed another substance, would have, for this purpose, to be separated from the intermicellar liquid by ultrafiltration, and the original total content of adsorbed substance and its amount in the filtered liquid would have to be determined. We will only refer to the example to be discussed later (p. 647), that in the dialysis of a saponin solution against one of methylene blue the dye collects in the saponin sol. The following observation of Osborne [6] is also to be explained in this way. If a calcium caseinate sol is dialysed against a dilute corrosive sublimate solution, the sublimate collects in the sol. Adsorption also frequently affords an interpretation, when a truly or semi-colloidally dissolved substance lowers the surface tension less in presence of a colloid than in its absence ; the concentration of the capillary-active substance is less because it is in part bound to the surface of the colloid particles. Thus, soaps lower the surface tension of water less when albumin or starch is present in the solution.[7]

Among biological processes many are to be found which can be represented as the adsorption of the micellæ of a hydrophilic sol upon other adsorbents, or as adsorption of smaller molecules by the micellæ of such a sol ; the adsorption of an agglutinin by bacteria,[8] of an opsonin by bacteria,[9]

[1] Biochem. Zeitschr. **23,** 27 (1909).

[2] Zentralbl. f. Bakteriol., Parasitenkunde, and Infektionskrankh. **40,** 265 (1905).

[3] Kolloidzeitschr. **2,** Supplementheft I, p. viii, and Supplementheft II, p. xi (1908).

[4] Zeitschr. f. physik. Chemie, **83,** 706 (1913).

[5] *loc. cit.* under [1].

[6] Journ. of Physiol. **34,** 84 (1906).

[7] *Berczeller,* Biochem. Zeitschr. **66,** 207 (1914).

[8] *W. Biltz,* Zeitschr. f. physik. Chemie, **48,** 615 (1904), according to measurements by *Eisenberg* and *Volk,* Zeitschr. f. Hygiene, **40,** 155 (1902) ; *G. Dreyer* and *J. S. C. Douglas,* Proc. Roy. Soc. **82,** B, 185 (1910) ; also *W. Biltz* and *Steiner,* Kolloidzeitschr. **7,** 120 (1910).

[9] *Ledingham,* Journ. of Hygiene, **12,** 320 (1912).

of a toxin by an antitoxin,[1] may be mentioned. The equilibria are established very rapidly, the adsorption isothermal holds; occasionally a saturation or a maximum in the adsorption isothermal has been observed.[2]

It is true that these processes are mostly distinguished by a property that is wanting in ordinary adsorption. They are strongly specific. Typhus-agglutinin is taken up to a large extent only by typhus bacteria, diphtheria toxin by diphtheria anti-toxin, etc. This is by no means in contradiction with the view of an adsorption, no matter whether it be regarded as a saturation of the last residual valencies, or whether it be brought into relation with the lowering of interfacial tension; for even in the last case the differential coefficient $\frac{d\sigma}{dc}$ in the Gibbs formula might depend specifically upon the nature of adsorbent and adsorbed substance. But it is certainly a gap in the theory of these phenomena that up to the present this specific adsorption has been shown only by substances formed in biological processes and not by those prepared in the test tube. The idea suggests itself that only an adsorbent of suitable geometrical form is able strongly to adsorb a substance which corresponds to it in spatial dimensions. In the biological process adsorbent and adsorbed substance are causally connected in the manner of their formation, so that their shape may very well be fitted to one another. In the laboratory it has not yet been possible to produce an adsorbed substance from an adsorbent which, in consequence of the mode of formation, has a particular spacial arrangement and is preferentially adsorbed.

That these adsorptions are not smoothly reversible may have various causes. In the first place chemical changes in adsorbed proteins are very frequent (cf. p. 536). Coagulation of the adsorbing micellæ may also occur, and therewith the formation of flakes of various sizes and descriptions; this may have the result, as in the case of the coagulation of hydrophobic sols (cf. p. 457), that it depends upon the rate at which adsorbent and adsorbed substance are mixed with one another. Höber and Gordon [3] explain the so-called Danysz phenomenon [4] thus: the same amount of antitoxin which, when added quickly, binds a definite amount of toxin, leaves some of it free when added slowly.

Apart from some measurements upon not very well defined sols undertaken by de Metz,[5] the *compressibility* of lyophilic sols has not yet been measured in a thorough and trustworthy manner.

The change in the *solvent power for gases*, and, no doubt connected with this, the favouring of supersaturation by colloidally dissolved substances, alluded to in the case of hydrophobic sols, are again met with in the case of hydrophilic sols. These were investigated by Findlay [6] and his co-workers in the case of solutions of gelatine and starch.

[1] The calculation of a series of cases (e.g. diphtheria toxin by antitoxin, ricin by antiricin) in *W. Biltz*, Biochem. Zeitschr. **23,** 37 *et seq.* (1909). Further also *W. Biltz*, Medizin.-naturwissensch. Archiv, **1,** 362 (1907); *Landsteiner* and *Reich*, Zentralbl. f. Bakteriol., Parasitenkunde und Infections-Krankh. **39,** 83 (1905); *Landsteiner* and *Stankovic, ibid.* **41,** 108 (1906); **42,** 353 (1906); *Landsteiner* and *Botteri, ibid.* **42,** 562 (1906); *Landsteiner* and *Raubitschek*, Biochem. Zeitschr. **15,** 33 (1909).

[2] *loc. cit.*, under [8], p. 537. [3] Beitr. z. chem. Physiol. u. Pathol. **5,** 432 (1904).

[4] Ann. de l'Instit. Pasteur, **16,** 331 (1902).

[5] Wied. Ann. **41,** 663 (1890).

[6] *loc. cit.* p. 367; further *Findlay* and *Shen*, Journ. Chem. Soc. **99,** 1313 (1911); *Findlay* and *G. King, ibid.* **105,** 1297 (1914); *Findlay* and *Howell, ibid.* **107,** 282 (1915).

The Viscosity and Rigidity of Lyophilic Sols

Viscosity is a property in which hydrophilic sols are, in general, clearly distinguished from hydrophobic sols. Even in very dilute solution they are often appreciably more viscous than water, while more concentrated solutions are quite viscid. We need only think of a gelatine solution as an example. This well-defined property may further be conveniently measured by means of an Ostwald viscosimeter. Hence no property has been used so extensively and precisely as viscosity to characterize lyophilic sols and to follow their changes.

Unfortunately the internal friction measured by means of the viscosimeter is not a physically well defined property of a lyophilic sol. This appears even in the fact that if the various methods of measuring viscosity, which give results in agreement with one another in the case of pure liquids and true solutions, are used for hydrophilic sols, values for the viscosity are obtained which differ widely from one another. Thus, Garrett [1] found that the viscosity of sols such as silicic acid and gelatine was much smaller when estimated by means of the time of outflow in the viscosimeter than when determined by means of the damping of an oscillating disc according to Grotrian [2] and König's [3] methods.

The difference amounts, even with a dilute silicic acid sol (0·81 per cent. SiO_2), to about 10 per cent., and the value determined by the method of damping may rise with a concentrated sol to many times that found by efflux; thus it amounts for a concentrated silicic acid sol (3·76 per cent. SiO_2) to 0·47 (at 18°; water equals 0·0105) with the method of damping, and to 0·18 (at 16°) with the efflux method; with a 3 per cent. glue solution to 0·022 (30°) as against 0·016 (at the same temperature).

To this we must add a number of other peculiarities and irregularities which Garrett points out. In gelatine sols the damping increases with time, without this being due to a change in the state of the sol. For, if the disc is removed, cleaned, and then again allowed to oscillate in the sol, the original initial value of the viscosity η, with the same subsequent rise, is obtained. The amplitude of the oscillations is of considerable influence; with gelatine the viscosity is greater for small amplitudes than for large. With silicic acid and protein sols the viscosity decreases, on the contrary, with decrease in amplitude. Vibration greatly influences the damping in the case of gelatine sols.[4]

Hatschek [5] and particularly W. R. Hess [6] and his co-workers were successful in discovering the cause of this behaviour. A number of hydrophilic sols, such as those of gelatine, many proteins, starch, etc., have a distinct rigidity. It is not sufficient to enable the liquid to assume a form independent of gravity like a solid body; but it shows itself by the

[1] "Über die Viskosität und den Zusammenhang einiger Kolloidlösungen." Diss., Heidelberg, 1903.

[2] Pogg. Ann. **157**, 130, 237 (1876).

[3] Wied. Ann. **32**, 193 (1887); as regards the calculation see *O. E. Meyer*, Pogg. Ann. **113**, 55, 193, 383 (1861).

[4] Also with starch sols [cf. *Samec*, Kolloidchem. Beihefte. **4**, 132 (1912)].

[5] Kolloidzeitschr. **13**, 88 (1913); see also *ibid.* **7**, 301 (1910); **8**, 34 (1911); **11** 280, 284 (1912); **12**, 238 (1913).

[6] Kolloidzeitschr. **27**, 154 (1920) (there also the data concerning the earlier investigation of *W. R. Hess*, which began in 1906); Pflüg. Archiv, **162**, 187 (1915); *Rothlin*, Biochem. Zeitschr. **98**, 34 (1919).

liquid answering to an external mechanical stress by an elastic reaction. This has been known for a long time, and Schwedoff,[1] Colin,[2] Rankine,[3] and especially Rohloff and Shinjo [4] have measured it. For this purpose they allowed a cylinder or sphere to dip into the interior of the sol, and turned it by means of a torsion head through a certain angle. The cylinder (or sphere) does not quite follow this rotation, since the elastic force of the sol strives to maintain the original state. From the angle representing the lag of the cylinder (or sphere), the magnitude of this force can be calculated. W. R. Hess [5] showed the existence of this elastic force in the following way. In the sol was a paddle wheel, which carried a small mirror upon its axis, which projected from the sol. The wheel was first given a turning moment, and the dying away of the turning motion was followed on the curve traced by a light ray, reflected from the mirror, on sensitive paper fixed to a rotating drum. Even with very viscous true solutions, such as an aqueous glycerine solution, the state of rest was reached quite definitely asymptotically. Not so in the case of hydrophilic sols. With these the end state was only reached after several strongly damped oscillations about the final position of rest. Now, as W. R. Hess remarks, the mechanical force which is active, under normal conditions, in the case of an oscillating disc, and also in that of the efflux from the capillary of a viscosimeter, is so small, that the rigidity of the sol, in addition to the internal friction, will always make itself felt. Hence not only the latter has to be overcome, but also the elastic reaction, and hence the pure viscosity is by no means measured by the velocity of efflux. Only when at higher rates of flow the friction greatly increases, is the rigidity overwhelmed by it to such an extent that the latter may be neglected in comparison to the former, and that the true viscosity is measured by means of the time of efflux. W. R. Hess therefore determined the times of efflux of hydrophilic sols and suspensions from capillaries under high-pressure gradients, and arrived at constant, true values of the viscosity from a certain sufficiently large velocity of flow; in this region of high-pressure gradients Poiseuille's law holds, but not at low-pressure gradients.[6] He uses an arrangement, in which the sol to be investigated is sucked from a container into a capillary tube; in order to have at once a relative measure of the viscosity, pure water is sucked up in a parallel capillary, under the same conditions, to a given mark.

Hatschek [7] had arrived in another way at the explanation of the contradiction between the various methods of measurement in the case of hydrophilic sols. He showed that the "viscosity" of a sol depends in a high degree upon the *velocity of shear*, while this is not the case with true solutions and most hydrophobic sols, as long as the velocity of shear remains below a certain maximum value, at which the formation of eddies sets in. In order to measure the viscosity with variation in the rate of shear he uses a method first described by Couette,[8] which he slightly modified.

[1] Journ. d. phys. (2), **8**, 341 (1889).
[2] Compt. rend. **116**, 1251 (1893).
[3] Phil. Mag. (6), **11**, 447 (1906).
[4] Physik. Zeitschr. **8**, 442 (1907).
[5] Pflüg. Archiv, **162**, 187 (1915).
[6] Concerning the failure of this law for suspensions such as blood see also *Rothmann*, Pflüg. Archiv, **155**, 318 (1914).
[7] *loc. cit.* p. 539.
[8] Ann. d. chim. et d. phys. (5), **21**, 433 (1890); see also *MacMichael*, Journ. of Industr. Engin. Chem. **7**, 961 (1915).

Since it is doubtless of fundamental importance to carry out such measurements on various sols, the arrangement may be described more in detail.

This viscosimeter is represented in Fig. 117. A hollow cylinder A, which has bevelled ends, is hung up by a torsion wire B, which is fixed to a strong bracket C. Coaxial with cylinder A is a second one D, which is filled with the liquid to be investigated. E is a water jacket. The bevelled ends of the open cylinder A have opposite to them two short fixed protective cylinders F and F′, closed at one end, so that a space of about 2 mm. remained between the ends. D rests upon a disc G, which can be turned mechanically. The mirror H allows the deflection experienced by cylinder A, when D and the liquid contained in it turn, to be measured. The cylinders F and F′ prevent the liquid turning within A, and remove the complicated disturbances which are caused by the ends, when instead of A a cylinder closed at both ends is used.

The theory of the apparatus shows that the turning moment experienced by the cylinder A is equal to the product of the viscosity, the angular velocity, and a constant of the apparatus. With pure liquids and true solutions the ratio of deflection to angular velocity is proportional to the viscosity.

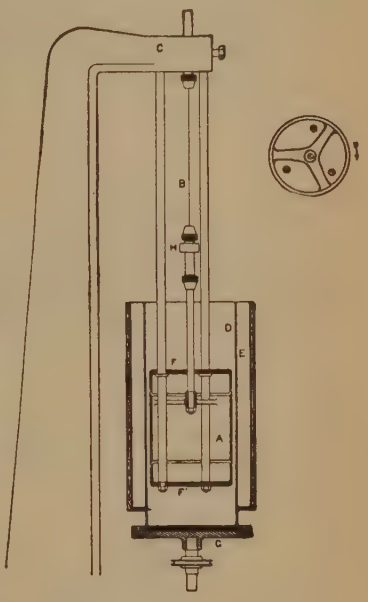


Fig. 117.

This was throughout the case, according to Hatschek's measurements, for water (until the angular velocity became so great that one had to reckon with eddies), but by no means so with gelatine sols. The viscosity, on the contrary, decreased greatly with increase in angular velocity; thus with a sol containing 5 grams of gelatine per litre, at 15·5° from 16 down to 7—the viscosity of water being unity—with a change in angular velocity of 5·1 degrees of arc per second to 93·9; 5·1 corresponds to one turn in 70·4 seconds, 93·9 to one in 3·83 seconds. A similar course was observed whether the measurements were begun with large or small angular velocities. A hysteresis was, however, distinctly present. Still more complicated was the behaviour of a starch sol, in which the viscosity—angular velocity curve showed a strong maximum.

It is immediately intelligible upon the basis of these measurements why, with the oscillating disc, larger "viscosities" are found at comparatively small rates of shear, than with the Ostwald viscosimeter, in which we are dealing with a larger rate of shear; and hence, as far as the behaviour of a sol is similar to that of a gelatine sol, the viscosity, measured in the viscosimeter, must be the smaller.

Hatschek's view, that with increase in angular velocity a definite, unalterable limiting value is reached, which corresponds to the true viscosity, is entirely correct according to W. R. Hess's results discussed above. Only, this limiting value will not, as Hatschek assumes, necessarily be reached in an Ostwald viscosimeter under ordinary experimental conditions; in its case as well the pressure gradient must be increased.

For the true viscosity η attained at high velocities of shear, Hatschek[1] deduced a relation which should hold for more concentrated sols and suspensions; it runs

$$\eta = \frac{\eta_M}{1 - \sqrt[3]{\varphi}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here η_M is the viscosity of the dispersion medium, φ the volume of the disperse phase contained in 1 c.c. of the sol. The theoretical assumptions which lead to this equation appear at first little probable.[2] Hatschek assumes that the micellæ are only separated by thin lamellæ of the intermicellar liquid, and that it is only a matter of the shearing of these lamellæ. This structure is one which we should at first like to ascribe only to a gel. In view of the great similarity between sols and gels (cf. p. 708), even with dilute sols, this at first improbable view is perhaps particularly accurate.

W. R. Hess,[3] under the assumption that the loss of energy upon the efflux of a suspension through a capillary is inversely proportional to the actual section of the liquid, arrived at a formula

$$\eta = \frac{\eta_M}{1 - \varphi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This does not agree with experience since the entire liquid cannot be regarded as flowing; before and behind each suspended particle immovable spaces of liquid must be imagined. He therefore improves the equation by introducing a factor β which depends both upon the size and form of the particles, and upon the velocity of shear, thus :—

$$\eta = \frac{\eta_M}{1 - \beta\varphi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This formula holds well for suspensions of blood corpuscles. As Hatschek[4] shows, formula (3) actually agrees with (1); the values of β found by Hess obey the relation

$$\beta = \frac{1}{\sqrt[3]{\varphi^2}}$$

as should be the case, if (3) is to be transformable into (1).

Hess and Rothlin emphasize that the objection may be raised against almost all previous measurements carried out with the Ostwald viscosimeter that they did not give true viscosities, but values falsified by the rigidity. Hence there is no guarantee that peculiarities observed in connexion with the "viscosity" may not be due to the neglect of the influence of rigidity. Without new measurements, taking this source of error into account, no decision can be come to as to what the departures from Einstein's formula (see p. 367),

$$\eta\varphi = \eta_M(1 + 2{\cdot}5\varphi),$$

which have frequently been observed, depend upon. They appear in two directions. The viscosity does not increase linearly with the volume

[1] Kolloidzeitschr. **8**, 34 (1911); **11**, 284 (1912); **12**, 238 (1913).
[2] *v. Smoluchowski*, Kolloidzeitschr. **18**, 192 (1916).
[3] Kolloidzeitschr. **27**, 1 (1920).
[4] Kolloidzeitschr. **27**, 163 (1920).

content, but much more rapidly for large contents; this was not only observed for more hydrophilic sols, such as sulphur sols, but also for hydrophobic ones (cf. p. 368). Then it is further found that sols of equal content, but with particles of different size, differ distinctly in viscosity, often in the sense that the sol with smaller particles is more viscous. Odén [1] found this to be the case with sulphur sols, in comparing such sols containing particles of about $10\mu\mu$ diameter with those containing particles of $100\mu\mu$ and over. According to Einstein's formula it should, on the other hand, only depend on the total volume of the disperse phase, and not on the size of the single particles, which does not enter into the formula. It is naturally not at all necessary that the divergences should be caused by the influence of the rate of shear. For as v. Smoluchowski [2] points out, the Einstein formula assumes that the micellæ are large compared with the sphere of molecular attraction, that they are present in small numbers, compared with the numbers of the liquid molecules, and that they are rigid solids; all conditions, that in lyophilic sols and in the sulphur sol referred to, are not necessarily fulfilled.

All regularities found for the "viscosity" appear uncertain and without sufficient support, since the measurements hitherto carried out are physically ill defined. Hence the regularity observed by W. Biltz,[3] that in the case of the dextrins the "viscosity" of the sols is clearly symbatic with the molecular weight (as measured by the osmotic pressure), is only given with caution. Thus, the viscosity of a 2 per cent. solution of amylodextrin with a molecular weight of 22,000 amounts to 1·545, that of an achroodextrin with a molecular weight of 1,200 in a solution of equal concentration to 1·034, and the viscosities of all dextrins with molecular weights lying between these values, arranged themselves, according to their molecular weights, between the two extremes. Since, however, according to Rothlin, gum arabic sols belong to the sols which obey Poiseuille's law even at ordinary pressure, this regularity does perhaps relate to the true viscosity.

It is no doubt likewise unobjectionable to use the "viscosity" obtained under conditions as similar as possible to draw qualitative conclusions as to the presence or absence of a substance in a sol, as Pauli does in the investigation of protein sols (see p. 572). He is guided by the idea that protein ions, and in general the large ions of a colloid electrolyte, give much more viscous solutions than non-dissociated colloids, for the reason that the hydration of these ions is probably much greater. It is here immaterial, in principle, whether the alteration depends upon a change in the forces of internal friction, or in the cohesive forces.

The close relation between hydroxide sols, such as those of Al_2O_3 and Fe_2O_3, and hydrophilic sols also appears in the fact that they show like peculiarities in viscosity, particularly when they are sufficiently concentrated. Such peculiarities were described by du Pré Denning [4] for concentrated Fe_2O_3 sols, and Gann [5] found that while with dilute, uncoagulated Al_2O_3 sols the efflux and damping methods gave approximately equal values for the viscosity, the values differed very greatly when the sol

[1] "Der Kolloide Schwefel," p. 102 *et seq.*
[2] *loc. cit.* p. 369.
[3] Zeitschr. f. physik. Chemie, **83**, 703 (1913).
[4] Ueber die Viskosität und die magnetische Doppelbrechung des Kolloidalen Eisenoxydhydrates." Diss., Heidelberg, 1904.
[5] Kolloidchem. Beiheft. **8**, 81 *et seq.* (1916).

became more viscous upon coagulation, and its particles therefore larger and richer in water. For a sol containing 0·651 g. Al_2O_3 per litre the calculated viscosity, before coagulation, was 1·03 by the efflux, and 1·08 by the oscillating disc method; on the conclusion of coagulation it was 1·32 by the first method, and 11·2 by the second. Here also it was necessary, therefore, to take the velocity of shear into account.

When, as will frequently be the case in the following pages, the "viscosity" of a sol is mentioned without further qualification, it will refer to that measured by the efflux method.

The Double Refraction of Lyophilic Sols

Another property which has been observed for a series of lyophilic sols is connected with the rigidity of hydrophilic sols, and hence also with the

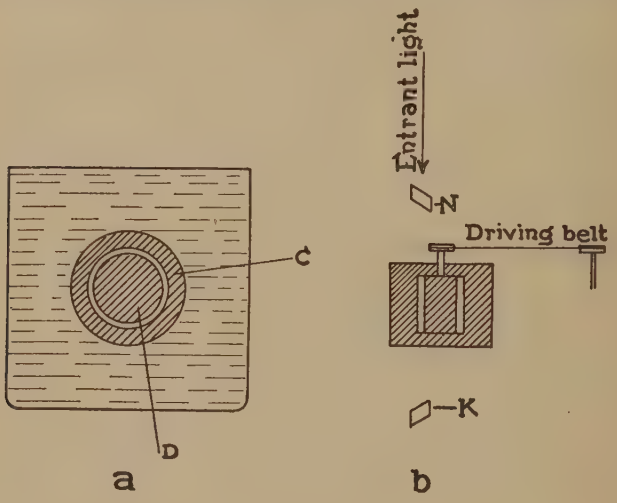


Fig. 118.

unusual behaviour of their "viscosity." Among these sols are found a number of liquids which become strongly doubly refracting under high mechanical stress. Kundt[1] was the first to follow up the following idea. An amorphous substance such as glass, i.e. a very viscous liquid, becomes doubly refracting under pressure. Hence the particles of a viscous liquid in the ordinary sense need not necessarily follow a mechanical displacement so quickly, that one might not be able to detect internal strain by suitable means from the double refraction. The experimental arrangement[2] can be seen from Fig. 118, in which *a* is a vertical section, *b* a horizontal section. C is a fixed hollow cylinder, in which the solid cylinder D turns. Its motion produces the mechanical displacement of the liquid in the annular space between C and D. A light ray polarized by the nicol N passes through the liquid and is analysed by a suitable arrangement (Babinet compensator

[1] Wied. Ann. **13**, 110 (1881).

[2] The arrangement corresponds in this form to that of *Umlauf*, Wied. Ann. **45**, 304 (1892).

K). Kundt, and later de Metz,[1] Almy,[2] and Hill [3] could not detect any double refraction with viscous liquids such as glycerine and sugar solutions. But a number of sols, such as those of gum tragacanth, cherry-gum, collodion showed double refraction; gelatine sols permitted the detection of a double refraction even in concentrations of 0·1 g. per litre. Hence it is again not the true viscosity that causes this phenomenon, for glycerine is some hundred times more viscous than so dilute a gelatine sol; it is rather connected with the circumstances that cause the unusual behaviour of the "viscosity." Probably the rigidity of the liquid as a whole is too small, and its mobility too great, to allow a double refraction to arise when it is subjected to moderate mechanical stress, and it is able to give way. With the Kundt arrangement, however, the possibility exists that the individual micellæ of the sol, which in part adhere to the wall of the resting, and in part to that of the rotating cylinder, may be stretched and thus become doubly refracting. Such distortions of the individual micellæ no doubt also play a part in the viscosity measurements, and cause the dependence, frequently complicated, upon the velocity of shear, as described by Hatschek (see p. 541); and also many peculiarities in the behaviour, described by Garrett, with oscillating discs.

That many substances show, in colloidal solution, a double refraction of the same sign as in the amorphous solid state, agrees with the assumption of distortion of the individual micellæ. Sols of tragacanth and cherry-gum have positive, and those of gum arabic, collodion, and gelatine negative double refraction (Umlauf [4]); the same difference in sign is found in the amorphous solid jellies of these substances (v. Ebner [5] and Herm. Ambronn [6]) (cf. also p. 722).

It is not possible to go into the details of these phenomena; they depend in a complicated manner upon the previous history of the sol and on other experimental conditions. It should perhaps be mentioned that the double refraction of gelatine sols treated in the same manner increases in proportion to the gelatine content (Hill [7]), and further, that it cannot be maintained from present data that all lyophilic sols show double refraction; Kundt could not observe any clearly marked effect with albumin sols. In any case, an investigation of this double refraction should extend and elucidate in striking fashion the results which would be obtained by measurements of the viscosity of such sols under known velocity of shear.

The explanation, to which preference is here given, of the double refraction of these hydrophilic sols, which assumes that it is caused by tension and compression, appears to me more probable than one in which it is regarded as equivalent to the stream double refraction of V_2O_5 and dye sols mentioned above, p. 408. In this latter case the slightest motion causes double refraction, because the micellæ are in the doubly refracting state at the outset and only require to be orientated. With the sols of gelatine and other substances much greater forces are required to produce double refraction. One might of course take up the position that, since the gelatine micellæ are only very slightly asymmetrical, the large forces

[1] Wied. Ann. **35**, 497 (1888).
[2] Phil. Mag. (5), **44**, 499 (1897).
[3] Phil. Mag. (5), **48**, 485 (1899); (6) **2**, 524 (1901).
[4] *loc. cit.* p. 544.
[5] "Untersuchungen über die Ursache d. Anisotropie organ. Substanzen." Leipzig, 1882.
[6] Wied. Ann. **38**, 159 (1889).
[7] Phil. Mag. (5), **48**, 490 (1899).

are necessary to orientate them in sufficient number. But nothing at present appears to me to favour such a view (cf. also p. 724).

Further, other sols, also hydrophilic, are known, which show stream double refraction, streak formation, etc., similarly to the hydrophobic sols named above; for example, many soap solutions,[1] the particles of which no doubt have a long narrow form (cf. p. 614).

Diffusion of the Particles of Lyophilic Sols

The methods employed in the case of hydrophobic sols for measuring the diffusion constant (see p. 370) are not, in general, applicable to the lyophilic sols, for the individual micellæ cannot usually be followed and counted under the ultramicroscope. Instead, the same methods may be used for lyophilic sols as for truly dissolved substances, which methods usually fail in the case of lyophobic sols, since the velocity of diffusion of their large micellæ is too small.

After diffusion had occasionally been investigated in the case of individual sols, R. O. Herzog[2] was the first to determine systematically the diffusion constants of a series of substances in hydrophilic sols. He used an arrangement due to Öholm[3] in which the dissolved substance diffused into the pure solvent, and the content of the layers at various levels was then determined. In most cases a definite diffusion constant could be calculated. If this could not be done with some substances, it was due to their not being homogeneous and to the sol containing particles of various sizes. In Table 143 a series of diffusion constants D measured by Herzog are given. For comparison the diffusion constants of some truly dissolved substances are also given.

The temperature coefficient for ovalbumin works out from the figures given at 0·028, a value which does not differ from that found for the diffusion of crystalloids.

We may now calculate from the diffusion constant, according to Einstein's formula (p. 350),

$$D = \frac{RT}{N}\,\frac{1}{6\pi r\eta} \qquad . \; . \; . \; . \; . \; . \; . \; . \; (1)$$

the radius of the particles, which are regarded as spherical. Ovalbumin gives a value of $2{\cdot}8\mu\mu$. If ovalbumin sols are not resolvable under the ultramicroscope, this depends accordingly not only upon the slight difference in refractive index between micellæ and intermicellar liquid, but also upon the small size of the micellæ.

In order to calculate the molecular weight one need only substitute the value of r so found into the equation

$$M = \frac{4}{3}\pi r^3 \varrho N \qquad . \; . \; . \; . \; . \; . \; . \; . \; (2)$$

There exists, it is true, an uncertainty regarding the density of the protein micella; it will lie between that of pure ovalbumin and of water. If one assumes a value of 1·1 as probable, M works out = 62,000. The assump-

[1] *Zocher, loc. cit.* p. 407.

[2] Zeitschr. f. Elektrochemie, **13**, 533 (1907); *R. O. Herzog* and *Kasarnowski*, Biochem. Zeitschr. **11**, 172 (1908); *R. O. Herzog* and *Polotzky*, Zeitschr. f. physik. Chemie, **87**, 449 (1914); Zeitschr. f. Elektrochemie, **17**, 679 (1911); also Kolloidzeitschr. **2**, 1 (1907).

[3] Zeitschr. f. physik. Chem. **50**, 309 (1905).

TABLE 143

Diffusion Constants of the Particles of Hydrophilic Sols

Substance.	t in deg.	$D\left(\frac{cm.^2}{sec.}10^5\right)$.
Ovalbumin	7·75	0·052
,,	15·5	0·063
Ovomucoid	7·75	0·039
Clupein sulphate	8·2	0·067
Pepsin	12	0·073
Rennin	16	0·071
Invertin	16·6	0·041
Emulsin	15·3	0·042
Urea (M = 60·04)	18	1·01
Glucose (M = 180·12)	18	0·57
Raffinose (M = 504·32)	18	0·355

tions made in applying equations (1) and (2), that the particles are spherical and large compared with the molecules of the dispersion medium, are doubtless approximately fulfilled.

If r be eliminated from equations (1) and (2), we obtain as relation between M, D and ϱ the equation deduced by Perrin [1] and R. O. Herzog [2]

$$\frac{MD^3}{\varrho} = \frac{R^3T^3}{162\pi^2N^2\eta^3} = \text{Const. (at constant temperature)} \quad . \quad (3)$$

This formula is best fulfilled for micellæ and for substances of high molecular weight, for which the assumptions just mentioned as underlying equations (1) and (2) are fulfilled. Herzog accordingly found it to be confirmed for sugars of fairly high molecular weight. For smaller molecules an equation

$$MD^2 = \text{Const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

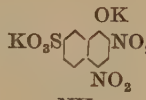
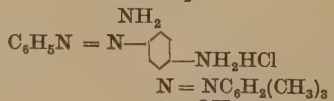
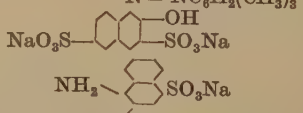
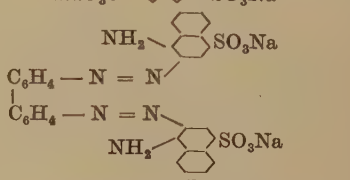
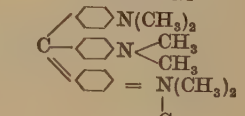
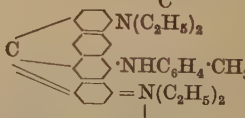
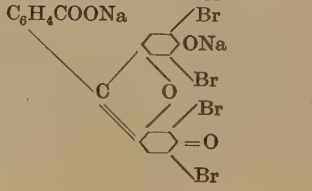
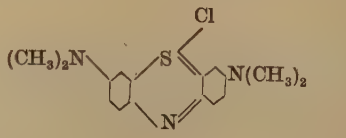
is frequently more nearly fulfilled. It is deduced from considerations put forward by E. Riecke,[3] and was first stated by v. Euler [4]; it does not assume that the dissolved particles are large compared with the molecules of the solvent, but only makes simplifying assumptions concerning the mean free path of the dissolved molecules. One might also deduce the molecular weight of ovalbumin from equation (4)—at 18° $MD^2 = 60 \times 10^{-10}$ for the crystalloids such as urea, etc., given in Table 143—the molecular weight of ovalbumin would then work out at about 20,000. But the assumptions made in formulæ (1) and (2) appear to be better fulfilled than those of (4).

With many substances, particularly dyes, investigated by Herzog, we are dealing with electrolytes, and therefore, in so far as their solutions are colloidal, with colloidal electrolytes. We have not therefore simply to consider a relation between molecular weight and diffusion constant, but must first of all take into account Nernst's [5] relation between the diffusion

[1] Ann. d. chim. et d. phys. (8), **18,** 93 *et seq.* (1909).
[2] Zeitschr. f. Elektrochemie, **16,** 1003 (1910).
[3] Zeitschr. f. physik. Chemie, **6,** 564 (1890).
[4] Wied. Ann. **63,** 273 (1897).
[5] Zeitschr. f. physik. Chemie, **2,** 613 (1888).

TABLE

Diffusion an

Dye.	Constitutional Formula.	Molecular Weight.
Naphthol yellow S		390
Chrysoidine		248·5
Ponceau 3 R		358
Congo red		696
Auramine		303·5
Crystal violet		443·5
Night blue		575·5
Eosin		692
Methylene blue		319·5

[1] Kolloidzeitschr. **3**, 76 (1908).
[2] Compt. rend. **150**, 619 (1910).
[3] *van Bemmelen*-Festschrift, p. 107 (1910).
[4] Zeitschr. f. physik. Chemie, **60**, 479 (1907).

14

ialysis of Dyes

Number of Atoms.	$D\left(\frac{cm^2}{sec.}.\ 10^5\right)$ in Water.	$D\left(\frac{cm^2}{sec.}.\ 10^5\right)$ in 5 per cent. gelatine.	Dialysis.
27	0·468(7·3°)	0·148(1·2°)	Naphthol yellow G: rapid. [Höber & Chassin,[1] Vignon,[2] W. Biltz [3]].
30	0·488(6·9°)	0·079(1·2°)	Rapid [Teague and Buxton[4]].
45	0·248(6·6°)	[0·0064(1·2°)][7]	Ponceau BO, 4 RD, 5 R: fairly rapid [W. Biltz[3]].
70	0·126(6·9°)	Extremely small	None [Teague and Buxton,[4] Vignon,[2] Biltz [3]].
43	—	0·132(1·2°)	Auramine O; rapid [Biltz[3]].
59	0·398(8·9°)	[0·016(1·2°)][7]	Not rapid [Freundlich and Neumann,[5] Vignon[2]].
84	—	Very small	None [Teague and Buxton,[4] Freundlich and Neumann,[5] Biltz[3]].
37	—	0·0333(1·2°)	Rapid [Teague and Buxton,[4] Vignon,[2] Biltz[3]].
39	—	0·0437(1·2°)	Rapid [Krafft and Preuner,[6] Teague and Buxton,[4] Biltz[3].]

[5] Kolloidzeitschr. **3**, 80 (1908).
[6] Ber. d. deutsch. chem. Ges. **32**, 1620 (1899).
[7] The brackets mean that the diffusion equation was not valid, and that a mean value of the "constants" observed was taken.

constant and the migration velocities of the two ions composing the electrolyte

$$\frac{1}{D} = \frac{1}{2RT}\left(\frac{1}{U} + \frac{1}{V}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Here U and V are the mobilities of the two ions. We can however conclude from these measurements with some degree of certainty at what size of particle, at what value of the diffusion constant therefore, a dissolved substance begins to behave like a colloid. A comparison of the diffusion constants of a considerable number of dyes with their power of dialysing through membranes showed, as was to be expected, an extensive parallelism between the two properties; this appears from Table 144, which is extracted from a table given by Herzog and Polotsky.[1] From it one also recognizes that diffusion in a gelatine gel goes throughout parallel with free diffusion. As will be discussed later (p. 728) diffusion in concentrated jellies (containing about 20 per cent. gelatine) is an exceedingly useful means of distinguishing colloidally dissolved substances from truly dissolved ones, or speaking more generally, of obtaining a certain measure of the size of the molecules or micellæ of the dissolved substance. This means is particularly convenient when, as in the case of coloured substances, the progress of diffusion can easily be followed. In a concentrated gel colloidally dissolved substances do not diffuse at all, while with increase in dialysability the rate of diffusion also decidedly increases. From these measurements the rule follows that in general a dye with a diffusion coefficient above $0{\cdot}2 \times 10^{-5}$ (at about 10°) dialyses rapidly. With a diffusion coefficient below this it nearly always dialyses slowly or not at all. A value of $0{\cdot}2 \times 10^{-5}$ would correspond according to formula (1) to a radius of the particle of about $0{\cdot}8\mu\mu$ and a M.W. of about 4,000. According to a rule pointed out by W. Biltz,[2] dyes with fewer than 45 atoms (or better, according to Herzog, 50 atoms) dialyse in general rapidly, and those with a larger number slowly or not at all.

These regularities probably hold for other classes of substance such as dextrins, polypeptides, salts of fatty acids, etc., in which one passes from the region of true into that of colloidal solutions, in ascending the homologous series, or, in general, when the molecular weight increases.

Perhaps no method is more fruitful for the investigation of lyophilic sols than the measurement of diffusion. If the velocity of diffusion of, say, a protein were investigated in solutions of various salts we might be able, in combination with the other chemical behaviour, to draw valuable conclusions from the increase or decrease in the size of the micellæ. The only difficulty is that the measurements are tedious—in view of the smallness of the diffusion constant they must be extended over 60 to 80 days—they are therefore impossible when the diffusing substances alter chemically-and always require the greatest attention to avoid the result being upset by the growth of micro-organisms.

A method which would give a result in a shorter time would greatly assist the investigation of lyophilic sols. Perhaps the determination of the diffusion constant with the aid of curved light rays,[3] in which the measurements only require to be extended over a few days, is also applicable here.

[1] *loc. cit.* p. 546.

[2] *van Bemmelen*-Festschrift, p. 107 (1910).

[3] *Thovert*, Ann. d. chim. et. d phys. (7), **26**, 366 (1902; Heimbrodt, Ann. d. Physik (4), **13**, 1028 (1904).

The Osmotic Pressure of Lyophilic Sols. Membrane Equilibria

According to present experience, the particles of lyophilic sols have in general a lower molecular weight than those of lyophobic. With lyophilic sols the range is apparently about 5,000 to several 100,000. But even these values are still far too great to allow of the convenient and accurate application of such comparatively insensitive methods as those of lowering of vapour pressure, rise of boiling-point, and depression of freezing-point. For a substance with a molecular weight of 20,000 the calculated depression of the freezing-point in aqueous solution with a concentration of 10 g. per litre is 0·001°. Hence by this method either no difference, or only a very small and uncertain one, can be observed. Among particularly trustworthy experiments may be mentioned those of Bruni and Pappadà,[1] who were unable to detect either a depression in the freezing-point or a lowering of the vapour pressure [2] in the case of carefully dialysed sols of silicic acid, albumin, and gelatine.

On the other hand the osmotic pressure must readily permit of measurement. In the above-mentioned example, in which the depression of the freezing-point only amounted to 0·001°, the osmotic pressure would be about 7 mm. of mercury or 10 cm. of water, and thus be conveniently measurable. It has in fact been known for several decades that the osmotic pressure of lyophilic sols can be determined. Th. Graham [3] drew attention to the fact; Pfeffer [4] measured the pressure of gum and glue solutions with his osmometer, Starling,[5] Rodewald and Kattein,[6] B. Moore and his co-workers,[7] Reid,[8] W. Biltz and his co-workers,[9] Lillie,[10] Sörensen,[11] and others have carried out measurements of this kind, in some cases on an extensive scale. If nevertheless we are able only in a few cases to draw fairly probable conclusions concerning the molecular weight, this is due to the difficulties, already alluded to on p. 376, which stand in the way of the interpretation and calculation of the measurements.

There is first of all the circumstance pointed out by Wo. Ostwald,[12] that in lyophilic sols the process of dissolution need not by any means have reached its end, that is to say, that the micellæ are not yet in their final state of imbibition, and still strive to take up more water; in the measurement of the osmotic pressure this attraction for water might be added to that caused by the pure osmotic pressure. Ostwald assumes that we may,

[1] Rend. R. Accad. d. Linc. (5), **9**, 354 (1900).

[2] *Gerike* [Kolloidzeitschr. **17**, 78 (1915)] finds a very slight lowering of the vapour pressure with gelatine sols.

[3] See among other places Lieb. Ann. **121**, 37 and 62 (1862).

[4] "Osmotische Untersuchungen," Leipzig, 1877.

[5] Journ. of Physiol. **24**, 317 (1899).

[6] Zeitschr. f. physik. Chemie, **33**, 586 (1900).

[7] *B. Moore* and *Parker*, Amer. Journ. of Physiol. **7**, 261 (1902); *B. Moore* and *Roaf*, Biochem. Journ. **2**, 34 (1906); other work summarized by *B. Moore* and *Roaf*, Kolloidzeitschr. **13**, 133 (1913).

[8] Journ. of Physiol. **31**, 438 (1904); **33**, 12 (1905).

[9] *W. Biltz* and *v. Vegesack*, *Wallach*-Festschrift, p. 152 (1909); Zeitschr. f. physik. Chemie, **68**, 357 (1910); **73**, 481 (1910); *W. Biltz*, *ibid.* **77**, 91 (1911); **83**, 625, 683 (1913); **91**, 705 (1916).

[10] Amer. Journ. of Physiol. **20**, 127 (1907).

[11] Zeitschr. f. physiol. Chemie, **106**, 1 (1919).

[12] *Wo. Ostwald* and *Mündler*, Kolloidzeitschr. **24**, 7 (1919).

in the first instance, apply the same formula to the taking up of water by the particles of the sol as holds for imbibition by these particles when in the gel state. The pressure required to force water out of an aqueous gel in equilibrium will be described as the swelling pressure P (cf. p. 673); equally large is the tendency of the gel to take up water at this pressure. For the dependence of P on the concentration of the gel—content of amorphous-solid substance per 1,000 c.c. of the gel—the relation

$$P = P_0 c_g^k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

holds. Here c_g is the concentration of the gel, P_0 and k are constants; the swelling exponent k usually lies between 2 and 3. Wo. Ostwald therefore assumes that a swelling pressure of just this kind, obeying formula (1), is active in the micellæ contained in the sol. The observed osmotic pressure P_b is then equal to the pure osmotic pressure P_0, increased by the swelling pressure P of the micellæ, hence

$$P_b = P_0 + P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or

$$P_b = RTc + P_0 c_g^k \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Here c is naturally the molar concentration of the micellæ in the sol, while c_g is the concentration of amorphous solid in the micellæ, calculated for the micellæ contained in unit volume.

Formula (3) has not hitherto been found to agree for lyophilic sols. Perhaps this depends upon the fact that these sols are also in other respects not in a state of equilibrium. Thus one frequently observes that the osmotic pressure changes when the sol is stirred or shaken.[1] What the cause of this is has not yet been determined. We might suppose that, as in the case of protein sols, fresh surface is formed on shaking, on which micellæ are adsorbed and denatured (cf. p. 535), or that a slow coagulation takes place in the sol, and stirring hastens the association of coarser particles (cf. p. 437). The limiting case might occur of the molar concentration of the sol being so small that the true osmotic pressure P_0 becomes negligible; the observed pressure would then be equal to the swelling pressure

$$P_b = P_0 c_g^k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It would thus be proportional to a power of the concentration of disperse phase in the sol. Wo. Ostwald points out that actually a series of measurements by J. Duclaux [2] on Fe_2O_3, ThO_2, and $Cu_2Fe(CN)_6$ sols (the intermicellar liquid pressed through an ultra filter served as external solution) and a series by W. Biltz [3] on Congo pure blue (as external liquid an electrolyte solution of the same conductivity) obey equation (4). The exponent k had values of about 3 as in the case of the swelling pressure.

In any case we may now say that we can only with certainty draw conclusions concerning the molecular weight of the micellæ from osmotic measurements of lyophilic sols, when the equation

$$P = RTc$$

[1] See e.g. *W. Biltz* and *v. Vegesack, loc. cit.* p. 551; *Lillie, loc. cit.* p. 551.
[2] Journ. Chim. Phys. **7**, 405 (1909).
[3] Zeitschr. f. physik. Chemie, **77**, 91 (1911).

is actually fulfilled for the osmotic pressure, that is, when the latter is proportional to the absolute temperature and to the concentration.[1]

A second important circumstance which has to be taken into account is the influence discovered by Donnan[2] of colloidally dissolved substances on the distribution of electrolytes, even of those easily dialysed, between internal and external liquid. Donnan's argument holds strictly, in the first instance, for colloidal electrolytes, amongst which, in particular, dyes such as Congo red, etc., may be included. In these cases one ion, in Congo red the anion, is so large that it does not pass through the membrane, while the corresponding kation, the Na ion, could easily dialyse if it were not held back by the anion ; the sol must, indeed, contain the same number of anions and kations. If, now, a second electrolyte which has one ion in common, for example NaCl, is present, it does not, as was originally believed, distribute itself in such a way between the external and internal liquid that its concentration is everywhere the same, but the colloid electrolyte exerts a strong influence in the sense of making the concentration of the NaCl larger in the external, and smaller in the internal liquid.

Let us suppose for the sake of simplicity that the electrolyte is fully dissociated, and that there is the same volume of liquid on both sides of the membrane. Table 145 gives a view of the initial and equilibrium states ; the vertical lines in the middle of each division of the table represent the membrane.

TABLE 145

Initial State.				Equilibrium State.				
Interior.		Exterior.		Interior.			Exterior.	
R′	$Na^{\cdot}$	Cl′	$Na^{\cdot}$	R′	Cl′	$Na^{\cdot}$	Cl′	$Na^{\cdot}$
c_1	c_1	c_2	c_2	c_1	x	$c_1 + x$	$c_2 - x$	$c_2 - x$

In the internal liquid there is thus originally only the colloid electrolyte with the anion R′ and the kation $Na^{\cdot}$, and in the outer liquid NaCl. At equilibrium the amount x of NaCl has passed from the exterior to the interior of the membrane. x cannot have any arbitrary value, but is determined by the condition that in equilibrium the same amount of work is required to transfer either dn mols of Cl′ ions or dn mols of $Na^{\cdot}$ ions from the interior to the exterior. These amounts of work are

$$- dn\mathrm{RT} \log \frac{(\mathrm{Cl}')_2}{(\mathrm{Cl}')_1}$$

and

$$+ dn\mathrm{RT} \log \frac{(\mathrm{Na}^{\cdot})_2}{(\mathrm{Na}^{\cdot})_1}.$$

[1] The relationships do not appear to be any simpler for colloidal solutions in organic dispersion media. *J. Duclaux* and Mme. *Wollman* [Compt. rendu, **152**, 1580 (1911)] found no simple proportionality between osmotic pressure and concentration in the case of colloidal solutions of nitrocellulose in acetone, using denitrated collodion skins as membranes.

[2] Zeitschr. f. Elektrochemie, **17**, 572 (1911).

Here $(Cl')_1$ and $(Na^{\cdot})_1$ denote the concentration in the internal liquid, and $(Cl')_2$ and $(Na^{\cdot})_2$ those in the external. We therefore obtain

$$(Cl')_1(Na^{\cdot})_1 = (Cl')_2(Na^{\cdot})_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If we substitute in (5) the values represented in Table 145, we find

$$x(c_1 + x) = (c_2 - x)^2$$

It follows from this that

$$x = \frac{c_2^2}{c_1 + 2c_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and

$$\frac{c_2 - x}{x} = \frac{c_1 + c_2}{c_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If c_2, the concentration of the foreign electrolytes, is small compared with c_1, the concentration of the colloid electrolyte, then it follows from (7) that

$$\frac{x}{c_2} = \frac{c_2}{c_1},$$

hence x is also small as compared with c_2; that is, but little foreign electrolyte passes from the external to the internal liquid. The colloidal electrolyte apparently inhibits its diffusion.

If on the contrary c_1 is small compared with c_2, (7) gives

$$\frac{c_2 - x}{x} = 1,$$

that is, the foreign electrolyte distributes itself evenly between internal and external liquid, as was originally supposed.

Table 146 gives a picture of how the distribution of the foreign electrolyte alters with the change in the ratio of the concentrations $c_1 : c_2$.

TABLE 146

Membrane Equilibrium in Presence of a Colloid Electrolyte

c_1 (original Concentration of the Colloid Electrolyte in internal Liquid).	c_2 (original Concentration of the foreign Electrolyte NaCl in external Liquid).	$\frac{c_1}{c_2}$	$100\frac{x}{c_2}$	$\frac{c_2 - x}{x}$
0·01	1	0·01	49·7	1·01
0·1	1	0·1	47·6	1·1
1	1	1	33	2
1	0·1	10	8·3	11
1	0·01	100	1	99

Even if the foreign electrolyte has no ion in common with the colloid electrolyte, the latter influences its distribution. We have relationships such as are represented in Table 147, to which it is only necessary to add that $z = x - y$. If c_1 is large compared with c_2, then, as a thermodynamic argument completely similar to the foregoing one tells us, the kation

of the foreign electrolyte, in this example the $K^{\cdot}$ ion, will pass over strongly from the external into the internal liquid; the anion, on the other hand in the case chosen (Cl'), only to an extremely small degree.

TABLE 147

Initial State.				Equilibrium State.							
Interior.		Exterior.		Interior.				Exterior.			
R'	$Na^{\cdot}$	Cl'	$K^{\cdot}$	R'	Cl'	$Na^{\cdot}$	$K^{\cdot}$	Cl'	$Na^{\cdot}$	$K^{\cdot}$	
c_1	c_1	c_2	c_2	c_1	y	$c_1 - z$	x	$c_2 - y$	z	$c_2 - x$,	

The displacement in the distribution of the foreign electrolyte by the colloidal electrolyte has the further consequence that the observed osmotic pressure P_b is not simply equal to the pure osmotic pressure P_0, which only depends upon the molar concentration of the colloidal electrolyte $2c_1$. Hence the simple relation

$$P_b = P_0 = RT2c_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

does not hold, but the osmotic counter-pressure of the foreign electrolyte P_f comes in, for which the relation

$$P_f = RT2\{c_2 - x - x\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

holds. The observed osmotic pressure is therefore

$$P_b = P_0 - P_f = 2RT\{c_1 - c_2 + 2x\} \quad . \quad . \quad . \quad . \quad (10)$$

and it follows from (8) and (10) that

$$\frac{P_b}{P_0} = \frac{c_1 - c_2 + 2x}{c_1} = \frac{c_1 + c_2}{c_1 + 2c_2} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

if the value of x is introduced from (6).

If c_2 is small compared with c_1, it follows from (11) that $P_b : P_0 = 1$; the true osmotic pressure of the colloidal electrolyte is measured. If, conversely, c_1 is small compared with c_2, then $P_b : P_0 = \frac{1}{2}$. Hence, in the limiting case, the observed osmotic pressure is, on account of the Donnan counter-pressure, one-half that of the pure osmotic pressure of the colloid electrolyte. The foreign electrolyte would thus lower the osmotic pressure of a colloid electrolyte. One might at first be surprised that one does not measure the true osmotic pressure in the case of the even distribution of the foreign electrolyte, when c_1 is small compared with c_2, since according to equation (6) x is almost equal to $\frac{c_2}{2}$, and hence P_f, according to equation (9), is nearly zero. But it must be remembered that when P_f is so small, P_0 is also small in consequence of the small value of c_1, so that the Donnan counter-pressure, although slight, forms a sensible fraction of the very small true osmotic pressure.

Donnan and his co-workers[1] were able to confirm the theory exten-

[1] *Donnan* and *Harris*, Journ. Chem. Soc. **99**, 1554 (1911); *Donnan* and *Allmand*, *ibid.* **105**, 194 (1914); *Donnan* and *Garner*, *ibid.* **115**, 1313 (1919).

sively, using quite different membrane equilibria; thus, for example, with a solution of Congo red—the Na salt of diphenyldiazo-naphthylaminesulphonic acid (cf. Table 144, p. 548)—and NaCl using a parchment membrane; with solutions of potassium and sodium ferrocyanide and solutions of NaCl and KCl respectively using a copper ferrocyanide membrane; with a solution of KCl and LiCl using a layer of amyl alcohol as membrane —LiCl dissolves in the latter, and so passes through; KCl does not. In the case of Congo red, for example, the internal liquid contained at equilibrium, besides Congo red, NaCl in a concentration of 0·0879 mols per litre; in the external liquid, which had originally consisted of pure water, NaCl was present to the extent of 0·0980 mols per litre. Equation (5) was not always fulfilled quantitatively, which was due either to the laws of solution not holding strictly, or to the membrane adsorbing the ions to different degrees. W. Biltz [1] also found that a series of his earlier measurements,[2] on other dyes such as Congo pure blue, brilliant Congo, etc., agreed with Donnan's theory.

Donnan and Harris [3] further found that the osmotic pressure of a Congo red solution is greatly lowered by increasing concentrations of NaCl and NaOH, and see in this a confirmation of the theory according to the foregoing argument. It must, however, be regarded as questionable whether the very generally observed lowering of the osmotic pressure of lyophilic sols by electrolytes is always to be referred to the Donnan effect. If this were so, then, as equations (9) to (11) show, for the case of a foreign electrolyte with a common ion (and the same is true if no common ion is present), the lowering in osmotic pressure should depend practically only upon the initial concentration (and upon the valencies of the ions) but not upon any specific quantities. But this does not appear to be the case. Lillie [4] has described the strong lowering of the osmotic pressure of protein sols by electrolytes and finds an unmistakable connexion with the lyotropic series of the anions. The explanation that the micellæ associate to larger groups under the influence of the electrolyte, forces itself upon one as particularly probable; this kind of coagulation of lyophilic sols is very closely connected, as we shall consider later (p. 576) with the lyotropic properties of electrolytes.[5] Dabrowski,[6] it is true, believes that he has observed that the velocity of diffusion of ovalbumin in ammonium sulphate solution is greater than in pure water; the molecular weight would thus be smaller than in pure water in contradiction with the explanation just discussed. It would be very desirable if these alterations in the osmotic pressure produced by electrolytes and other foreign substances could be tested by independent means, such, for example, as the measurement of the velocity of diffusion. Even then, however, a connexion with lyotropic properties would be expected, if the lowering of the osmotic pressure by electrolytes were not connected with purely osmotic phenomena, but with the imbibition processes assumed by Wo. Ostwald (see p. 551).

The foregoing discussion shows how extremely difficult it is to interpret

[1] Zeitschr. f. physik. Chemie, **83,** 625 (1913).
[2] *W. Biltz* and *v. Vegesack,* Zeitschr. f. physik. Chemie, **73,** 481 (1910); *W. Biltz, ibid.* **77,** 91 (1911); see also *Bayliss,* Proc. Roy. Soc. **84,** B, 250 (1911).
[3] *loc. cit.* p. 585.
[4] *loc. cit.* p. 551.
[5] See also *Sörensen, loc. cit.* p. 551.
[6] Bull d. l'Acad. d. Scienc. d. Crac. 1912, p. 485.

the osmotic phenomena of lyophilic sols. It is therefore intelligible that only in rare cases can the conclusion concerning the molecular weight of the colloidally dissolved substance be to some extent regarded as certain.

In a high degree this is true of *hæmoglobin* in aqueous solutions according to measurements by Hüfner and Gansser.[1] That we are dealing with a pure osmotic pressure follows, in the first place, from the close proportionality with the hæmoglobin content of the solutions, and then from the fact that the molecular weight found in this way may be confirmed with great probability in other ways. Parchment thimbles were used as semipermeable membranes. For ox hæmoglobin in 10·8 per cent. solution at 1° C. a pressure of 109 mm. of mercury was found, giving a molecular weight of 16,300. The molecular weight may also be estimated in the following way. Hæmoglobin combines with carbon monoxide to form carboxyhæmoglobin, 1 gram of ox hæmoglobin taking up 1·338 c.c. at 0° and atmospheric pressure, that is, 0·00167 g. CO. If we assume that 1 mol of hæmoglobin combines with 1 mol of CO, we obtain a molecular weight of 16,700; and practically the same value is obtained when we assume that only one atom of iron is present in hæmoglobin, and calculate the molecular weight from the iron content (0·336 per cent.).

This is, as Zsigmondy [2] rightly emphasizes, the first case in which the micella of the hæmoglobin sol, characterized colloidally by means of dialysis, has shown itself identical with the molecule of hæmoglobin considered chemically. The solution of hæmoglobin therefore has colloidal properties because its molecular weight is so large. From the molecular weight thus found the radius of the hæmoglobin molecule, supposed spherical, can be calculated from the formula frequently employed (see p. 546)

$$M = \frac{4}{3}\pi r^3 \varrho N$$

as about $1{\cdot}7\mu\mu$; it has therefore actually the size of many particles of colloidal solutions, such as those of amicronic gold sols (cf. p. 504).

Sörensen,[3] on the basis of very extensive and careful experiments, in which he takes especially into account the Donnan theory and a possible coarsening of the micellæ, but not a tendency to imbibition, which is possibly present, arrives at the result that an ovalbumin solution in ammonium nitrate solution of a given composition (about 15 per cent.) has a definitely fixed osmotic pressure. He calculates from this a molecular weight of about 34,000 for water-free egg albumin. In order of magnitude this corresponds to the value of about 60,000 found by diffusion in pure water (cf. p. 546). With an albumin from horse serum W. Biltz [4] obtained a molecular weight of about 50,000, with samples of gelatine prepared by various methods values between 5,000 and 30,000; Boyle's law was approximately fulfilled by them.

W. Biltz [5] was also able successfully to determine the molecular weights of a number of *dextrins*. They mostly lay between 1,000 for a dextrin β, and 22,000 for an amylo dextrin. With some of them the requirement

[1] Engelmanns Arch. f. Physiol, Physiol. Abt. 1907, S. 209; see also *Hüfner, ibid.* 1894, p. 130; 1903, p. 217.
[2] "Kolloidchemie," 3rd Ed., p. 382.
[3] *loc. cit.* p. 551.
[4] Zeitschr. f. physik. Chemie, **91**, 705 (1916).
[5] Zeitschr. f. physik. Chemie, **83**, 683 (1913).

of proportionality between osmotic pressure and molecular weight was completely fulfilled. The deviations which appeared in other cases could be explained on the grounds that in the case of concentrated solutions the osmotic equilibrium was reached from below only slowly. Among the dextrins we also have cases which have been tested by other methods; Table 148 gives a comparison between the Biltz values and the values of Lintner and Düll [1] obtained by the freezing-point method, and a value of Öholm's,[2] calculated from the diffusion constants.

TABLE 148

Molecular Weights of Dextrins

Substance.	Molecular Weight from Osmotic Pressure.	Comparative Value.
Amylodextrin (mean) . .	21,350	18,000 (Lintner and Düll)
Erythrodextrin IIa . . .	3,000	2,900 ,, ,,
Achroodextrin I	1,800	1,970 ,, ,,
		1,800 ,, ,,
		2,100 ,, ,,
Dextrin β	950	972 calc. from formula $(C_6H_{10}O_5)_6$
Commercial dextrin (mean)	5,500	4,440 (Öholm)

The behaviour of Congo red solution is very difficult to explain. Bayliss [3] found from measurements of osmotic pressure a molecular weight that amounted to 97 per cent. of the theoretical value (696), as if the Congo red were dissolved in the form of undissociated molecules; W. Biltz and v. Vegesack [4] and Donnan and Harris [5] were able to confirm this. But according to conductivity measurements by these investigators the Congo red is practically completely dissociated; the molecular weight should therefore be half as great, the osmotic pressure twice as large. In explanation of this, Biltz suggests, no doubt correctly, that the particles have a molecular weight which is, in reality, a multiple of the simple M.W., and hence that the value of nearly 700 is a consequence of dissociation. This is in agreement with the fact that the diffusion constant is much smaller than a molecular weight of 700 would require; it amounts (at 6·9°) to $0{\cdot}126 \times 10^{-5}$, while e.g. erythrosin B with a M.W. of 800 and the smaller number of atoms (37 instead of 70 for Congo red) has a diffusion constant of $0{\cdot}265 \times 10^{-5}$ (at 6·6°).[6] We should conclude from formula (4), p. 547,

$$MD^2 = \text{Const.}$$

that the M.W. of Congo red should be about 3,000. It is true that, in order to explain the conductivity, we should then have to ascribe to the larger ions a comparatively large migration velocity. This agrees, however,

[1] Ber. d. deutsch. chem. Ges. **26**, 2533 (1893); **28**, 1522 (1895).
[2] Zeitschr. f. physik. Chemie, **70**, 378 (1910).
[3] Proc. Roy. Soc. **81**, B, 269 (1909); **84**, 229 (1912); Kolloidzeitschr. **6**, 23 (1910).
[4] Zeitschr. f. physik. Chemie, **73**, 481 (1910).
[5] *loc. cit.* p. 555.
[6] According to measurements by *R. O. Herzog* and *Polotzky*, *loc. cit.*, p. 546.

with data derived from other colloid electrolytes (cf. p. 566).[1] The Congo red solution is not resolvable in the ultramicroscope. The solution of the dye-acid, Congo blue sol, is generally [2] resolvable, and gives according to Bayliss a much lower osmotic pressure, which would lead to a M.W. of about 14,000. Since the acids are in general much more weakly dissociated, the influence of dissociation will also make itself far less felt here.

Moore and Roaf [3] found no osmotic pressure with sols of starch, tragacanth, and silicic acid. Samec [4] found values for *starch* leading to a M.W. of 100,000.

That the rise of osmotic pressure proportionally to the absolute temperature is an important characteristic sign of a purely osmotic effect, has already been mentioned. With gelatine sols it increased faster than proportional to the absolute temperature,[5] no doubt because the micellæ became smaller with rise of temperature (cf. p. 704).

It is notable that many substances which give colloidal solutions in water, with M.W. of some 1,000 and more, are truly dissolved in organic liquids, and show M.W.'s corresponding to their constitutional formulæ. Thus, for example, the soaps,[6] and also the counterpart of a soap, the salt of an amine of high molecular weight,[7] hexadecylamine chloride, $C_{16}H_{33}NH_2 \cdot HCl$, which behaves in water like a soap, all have simple molecular weights in alcohol; tannin gives, when dissolved in glacial acetic acid, a depression of the freezing-point corresponding to the simple molecular weight.[8] The same is true of many dyes.[9] Their solutions in organic solvents show also in other respects the usual behaviour; the dissolved substance diffuses through membranes, raises the surface tension of the solvent,[10] and so on.

Concerning the measurement of osmotic pressure, the most important points have been noted earlier (see p. 377). Sörensen [11] has worked out a method for determining the counter-pressure which is just necessary to prevent a motion of the liquid through the membrane.

Further Consequences of Donnan's Theory of Membrane Equilibrium

If the solution of a colloid salt, say Congo red, be dialysed against pure water, the $Na^{\cdot}$ ions strive to pass through the membrane. This is only possible when OH' ions also pass through, that is, one observes a hydrolysis of the salt. The initial and final states may be represented as in Table 149 if we again assume complete dissociation and equal volumes upon both sides of the membrane.

[1] This explanation appears to me more probable than that which *Donnan* and *Harris* [Journ. Chem. Soc. **99**, 1567–1568 (1911)] prefer, namely, that the $Na^{\cdot}$ ion, for reasons difficult to follow, does not take part in the formation of the osmotic pressure.

[2] *Hantzsch* [Ber. d. deutsch. chem. Ges. **48**, 158 (1915)] succeeded in also preparing non-resolvable Congo acid solutions.

[3] *loc. cit.* p. 551.

[4] *Samec* and *v. Hoefft*, Kolloidchem. Beiheft. **5**, 195 *et seq.* (1913).

[5] *Moore* and *Roaf*, *loc. cit.* p. 551.

[6] *Krafft* and *A. Stern*, Ber. d deutsch. chem. Ges. **27**, 1747, 1755 (1894); *Krafft* and *Wiglow*, *ibid.* **28**, 2566, 2573 (1895); *Krafft* and *Strutz*, *ibid.* **29**, 1328 (1896); *Krafft*, *ibid.* **32**, 1584, 1596 (1899); Miss *Laing*, Journ. Chem. Soc. **113**, 435 (1918).

[7] *Krafft*, Ber. d. deutsch. chem. Ges. **29**, 1331 (1896).

[8] *Paternò*, Zeitschr. f. physik. Chemie. **4**, 457 (1889).

[9] *Krafft*, Ber. d. deutsch. chem. Ges. **32**, 1610 (1899).

[10] See *Freundlich* and *Neumann*, *loc. cit.* p. 549.

[11] Zeitschr. f. physiol. Chemie, **106**, 43 *et seq.* (1919).

TABLE 149

Initial State.			Equilibrium State.				
Interior.		Exterior.	Interior.			Exterior.	
R′	Na·	Pure water	R′	Na·	H·	OH′	Na·
c_1	c_2		c_1	$c_1 - x$	x	x	x

By means of a thermodynamical argument such as that on p. 553, we obtain

$$\frac{c_1 - x}{x} = \frac{x}{(\mathrm{OH}')_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $(\mathrm{OH}')_1$ is the OH′ ion concentration in the interior. Now the relation

$$x(\mathrm{OH}')_1 = \mathrm{K_W} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which $\mathrm{K_W}$ is the dissociation constant of water, holds in the interior. From (1) and (2) it therefore follows that

$$x^2 = \mathrm{K_W}(c_1 - x)$$

or, if x be neglected in comparison with c_1,

$$x = \sqrt[3]{\mathrm{K_W} c_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Since $\mathrm{K_W} = 10^{-14}$, x becomes small under these conditions. It becomes much larger when the volume of the external liquid is greater. If this, for example, is V times greater, then the concentrations of Na· and OH′ ions in the external space become, at equilibrium, equal to $\frac{x}{\mathrm{V}}$ and $\frac{(\mathrm{OH}')}{\mathrm{V}}$, and equation (3) becomes

$$x = \sqrt[3]{\mathrm{K_W} \mathrm{V}^2 c_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

A *membrane hydrolysis* of this kind may frequently be observed. A Congo red solution becomes darker and more turbid with protracted dialysis. The original colour is restored by boiling in a glass vessel. According to Donnan and Harris [1] this depends upon nothing else than the formation, during dialysis, of some of the dye acid; and the neutralization of this hydrolytically separated acid by the alkali of the glass. For, if the Congo red solution is dialysed against dilute alkali instead of pure water, no change in the deep red colour is observed, even with long-continued dialysis. A similar explanation applies to the corresponding observations of W. Biltz and v. Vegesack [2] on benzopurpurin.

If the acid of the colloidal electrolyte (or its base, as the case may be) is difficultly soluble or only slightly dissociated, the membrane hydrolysis is greatly increased. In the case of a slight dissociation of the acid, the distribution at equilibrium with equal volumes is as represented schem-

[1] Journ. Chem. Soc. **99**, 1560 *et seq.* (1911).
[2] Zeitschr. f. physik. Chemie, **68**, 357 (1910).

TABLE 150

State of Equilibrium.					
Interior.				Exterior.	
HR	R′	OH′	Na·	OH′	Na·
y	$c_1 - y$	$y - x$	$c_1 - x$	x	x

atically in Table 150. The calculation leads to the result

$$x = \sqrt[3]{\frac{K_W}{K_S} c_1^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where K_S is the dissociation constant of the acid.

The hydrolysis produced by the action of the membrane is stronger than if the colloidal electrolyte were equally distributed in the total volume (internal + external liquid). For, if $c_1 = 1$ and $K_S = 10^{-8}$, we have from equation (5) a value of $100x = 1$ per cent.; from the ordinary equation for hydrolysis

$$\frac{x^2}{1 - x} \frac{c_1}{2} = \frac{K_W}{K_S}$$

$100x = 0{\cdot}14$ per cent. This is intelligible when we consider that, in the external liquid, the Na· and OH′ ions are much farther removed from the R′ ions and HR molecules, and are separated by a diffusion path with more hindrances in it; the equilibrium, imagined as kinetic, is entirely other than if the R′ ions and HR molecules were evenly distributed in the whole volume of the liquid.

The Donnan distribution results in the formation of *membrane potentials*.[1] This is intelligible when we consider that we have, in equilibrium, one and the same electrolyte in different concentrations on the two sides of the membrane. As an example the one given on p. 553 of the colloid electrolyte NaR with NaCl as foreign electrolyte may be considered. If $\varepsilon_1 - \varepsilon_2$ is the difference between the potentials on the two sides of the membrane, then $F(\varepsilon_1 - \varepsilon_2)$ is the electrical work of transference of one F (96,540 coulomb) through the membrane. This corresponds osmotically to a work

$$pRT \log \frac{(Na\cdot)_2}{(Na\cdot)_1} + qRT \log \frac{(Cl')_1}{(Cl')_2},$$

where p and q are the transport numbers of kation and anion. According to equation (5), p. 554,

$$\frac{(Na\cdot)_2}{(Na\cdot)_1} = \frac{(Cl')_1}{(Cl')_2} = \lambda.$$

Further,

$$p + q = 1.$$

[1] *Donnan*, Zeitschr. f. Elektrochemie, **17**, 579 (1911).

From which follows the formula

$$\varepsilon_1 - \varepsilon_2 = \frac{RT}{F} \log \lambda$$

for the potential difference. Donnan and Green [1] tested it for the fundamentally similar case, in which a membrane is bounded by two differently concentrated solutions of a salt which does not pass through the membrane; they used a membrane of copper ferrocyanide and solutions of potassium ferrocyanide. The agreement between observation and calculation was such that the divergences found could be referred to uncertainties in the knowledge of the dissociation of the salt and the mobility of its ions.

Between colloid electrolytes, which have an ion with a M.W. of 3,000 to 100,000, and the micellæ of hydrophobic sols with their adsorbed active electrolytes having M.W.'s of 1,000,000 and more, no fundamental distinction can be drawn. A difference will be present in so far as, in the case of the micellæ of the hydrophobic sol, the oppositely charged ions mainly arrange themselves around the large micellæ with their very considerable charge, whereby an electrical double layer comes into being, whereas with ordinary electrolyte solutions and further also with colloid electrolyte solutions, the lines of force proceeding from the ions will be distributed much more irregularly. But even with a hydrophobic sol the ion of a foreign electrolyte, and the common ion of the active electrolyte, will be able to dialyse through a membrane, and to remain in the interior liquid to an extent depending upon the concentration of the micellæ. One will hardly hesitate to apply Donnan's views here as well. In this case the molar concentration of the "colloidal electrolyte," that of the micellæ, will often be small compared with that of the foreign electrolyte. The case is thus that in which c_1 is small compared with c_2; the foreign electrolyte therefore distributes itself fairly evenly between internal and external liquid. But the observed osmotic pressure is, in this case, greatly different from the pure osmotic pressure of the micellæ (cf. p. 555). We can therefore hardly draw conclusions as to the molecular weight of the micellæ from the observed osmotic pressure. For this reason we refrained earlier (p. 377) from drawing conclusions in this direction from the measurements of J. Duclaux and others.[2]

The Optical Properties of Lyophilic Sols

Lyophilic sols show the Tyndall phenomenon more or less strongly; no effect, or only a faint one, is given by sols such as those of the many dextrins, the particles of which are also small according to osmotic measurements; while a stronger effect is produced by sols such as those of the many proteins, gelatine, etc., in which larger particles may be assumed. The strength of the Tyndall light has sometimes been determined by photographing it and measuring the blackening,[3] a method which with many lyophilic sols allows conclusions to be drawn concerning their micellæ.

In most cases lyophilic sols cannot be readily resolved in the ultramicroscope. This depends just as much upon the particles being in many cases too small, as upon the difference in refractive index being too slight

[1] Proc. Roy. Soc. **90**, A, 450 (1914).
[2] *loc. cit.* p. 377.
[3] *Arisz*, Kolloidchem. Beiheft. **7**, 22 *et seq.* (1915).

(see p. 387). One then sees under the ultramicroscope only a Tyndall cone, or the liquids are optically empty.

A question which suggests itself is: how is the transition to true solutions shown in the Tyndall phenomenon? Strictly speaking this question is not justifiable. For, as will be discussed more in detail later (cf. p. 775), the molecules of the solvent, as well as those of the truly dissolved substance, suffice to scatter the light. It is only a question as to whether a sufficiently powerful beam of light can be provided, and whether coarser impurities such as dust or colloidal foreign substances, which scatter strongly, can be removed sufficiently completely. If the means are increased in power, the apparent limit at which the Tyndall light is just observable will be greatly extended. We can in reality only inquire at what size of particles the Tyndall beam appears with the light intensity usually applied, say that of an arc-lamp.

Spring [1] and Lobry de Bruyn [2] believed that they had already observed this limit. A necessary preliminary is the provision of a method by which the coarser impurities above mentioned can be so completely removed that optically empty liquids are obtained. The investigators above named believed that they had found two ways of attaining this end. In one, they removed colloid and dust particles by kataphoresis. It appears still more effective to produce a very gelatinous precipitate, say of $Zn(OH)_2$, in the liquid, which as it settles carries down the particles of impurity. According to their statements they obtained optically empty water and aqueous solutions of salts of the alkalis and alkaline earths. On the other hand they observed a Tyndall beam in 5 to 50 per cent. solutions of cane sugar and raffinose. They believed that the conclusion could be drawn from these experiments that the larger molecules of these substances are already large enough compared with the water molecules to produce the Tyndall effect. Le Blanc and Kangro [3] could not confirm these investigations. They could not obtain optically empty liquids by the means employed by Spring and de Bruyn. Le Blanc and Wolski [4] succeeded in doing so later by ultrafiltering the liquids in a suitable manner, using as ultrafilter a piece of old taffeta soaked in a 1 per cent. alcoholic collodion solution. The ordinary collodion filter, in which the collodion film is prepared on paper, was not found suitable. To test for optical emptiness they used the slit ultramicroscope, with an arc-lamp as source of light. Under these conditions not only was water rendered optically empty—neither the path of the light nor single particles could be seen when in 5 minutes 2 c.c. flowed through the observation cell, and hence 7 c.mm. were directly observed—but the solutions of inorganic salts, acids, and bases, and concentrated solutions of organic substances, such as citric acid, sugar, etc., could also be rendered optically empty. This is quite to be expected under the optical conditions in question (cf. p. 775).

Many hydrophilic sols, such as those of silicic and stannic acids, starch, many proteins and their degradation products, are colourless. The connexion which possibly exists between the colour of dye solutions and their colloidal properties will be dealt with later (see p. 651).

[1] Rec. d. Trav. Chim. d. Pays-Bas, **18**, 153, 231 (1899).

[2] *Lobry de Bruyn* and *L. K. Wolff*, Rec. d. Trav. Chim. d. Pays-Bas, **23**, 155 (1904).

[3] Zeitschr. f. Elektrochemie, **19**, 794 (1913); Zeitschr. f. physik. Chemie, **87**, 257 (1914).

[4] Ber. d. Sächs. Akad. d. Wiss., Leipzig, 1920, p. 24; *Wolski*, Kolloidchem. Beiheft., **13**, 137 (1920).

Conductivity and Kataphoresis of Hydrophilic Sols

As regards conductivity and kataphoresis the hydrophilic sols differ very distinctly from the hydrophobic. Owing to their sensitivity to electrolytes, the conductivity of hydrophobic sols can rarely be investigated over a considerable range of concentration. We are usually dealing with the pure sols, the slight conductivity of which is almost entirely due to foreign electrolytes. The kataphoresis, on the other hand, is usually strongly marked and readily measurable, and allows extensive conclusions to be drawn concerning the conditions of stability. In principle, nothing stands in the way of regarding the micellæ as electrolytes, with the charged colloid particles as one kind of ion and the ions which form the external coating of the double layer as the other. But the hydrophobic sol differs, as has frequently been emphasized, quite clearly from an ordinary electrolyte solution. Compared with the number of ions in an electrolyte solution, the number of micellæ is small, their charge on the other hand large (cf. p. 393). We have a comparatively small number of individual, strongly charged nuclei, enveloped in layers of oppositely charged ions.

With hydrophilic sols, on the other hand, high conductivities can generally be measured: either, together with the micellæ of a colloidal non-electrolyte, foreign electrolytes, which will generally interact in some way or another with the colloid particles, are present in large concentrations; or we have the solution of a colloidal electrolyte, in which the ions of one kind are so large that they dialyse only slightly or not at all, while their number and the size of their charge are such that the conductivity is large and conveniently measurable and the relationships are like those in ordinary electrolyte solutions.

The measurement of the kataphoretic migration velocity is, on the other hand, more difficult than for hydrophobic sols. The particularly trustworthy ultramicroscopic methods fail, since the individual particles cannot usually be seen in the ultramicroscope. Macroscopically also the motion of the boundary often cannot be followed with Burton's apparatus, because the sol has no decided colour, or because the degree of turbidity or the difference in refractive index is too small. An arrangement described by L. Michaelis [1] is best suited for following the kataphoresis in lyophilic sols, since it remains, without further modification, applicable to higher electrolyte concentrations. It is similar to the experimental arrangement of Coehn (cf. p. 244), only that reversible electrodes (such as Zn in $ZnSO_4$ solution) dip into the two limbs of the U-tube. The bent tubes containing liquid, which lead in the current, are themselves filled with pure water, as are the limbs of the U-tube above the stopcocks. A connecting tube provided with a stopcock allows the levels of the liquid to be brought to equality.

McBain and his co-workers [2] have thoroughly investigated the con-

[1] Biochem. Zeitschr. **16,** 84 (1909).

[2] *McBain* and Miss *Taylor,* Ber. d. deutsch. chem. Ges. **43,** 321 (1910); Zeitschr. f. physik. Chemie, **76,** 179 (1911); *McBain,* III, B.A. Rep. on Coll. Ch., p. 2 *et seq.* (1920). *Bowden,* Journ. Chem. Soc. **99,** 191 (1911); *McBain,* Miss *Cornish,* and *Bowden, ibid.* **101,** 2042 (1912); *McBain,* Kolloidzeitschr. **12,** 256 (1913); *Bunbury* and *H. E. Martin,* Journ. Chem. Soc. **105,** 417 (1914); *McBain* and *H. E. Martin, ibid.* **105,** 957 (1914); Miss *Laing, ibid.* **113,** 435 (1918); *McBain* and *Bolam, ibid.* **113,** 825 (1918); *McBain,* Miss *Laing,* and *Titley, ibid.* **115,** 1279 (1919); *McBain* and Miss *Taylor, ibid.* **115,** 1300 (1919); *Salmon, ibid.* **117,** 530 (1920); *McBain* and *Salmon,* Journ. Amer. Chem. Soc. **42,** 426 (1920); Proc. Roy. Soc. **97,** A, 44 (1920).

ductivity of solutions of distinctive colloid electrolytes, the *soaps*, and elucidated it to a great extent. It is probable that the relationships found are typical of many, if not all, electrolytically dissociated hydrophilic sols; they will therefore be dealt with in detail.

Soap solutions show a strong conductivity, which adjusts itself throughout sharply and reversibly with changes in concentration and temperature when suitable precautions are taken in working; it is best to employ silver vessels, to avoid disturbances due to the alkali of the glass. In Table 151 the specific and molar conductivities λ and Λ of sodium palmitate solutions of various concentrations are given, and in Fig. 119 the molar conductivities Λ, at 90°, of solutions of the potassium salts of fatty acids, rising from the lower to the higher ones; the Λ values are plotted as ordinates against the molar concentrations as abscissæ. Curve 1 relates to K acetate, 2 to K hexoate (C_6), 3 to K decoate (C_{10}), 4 to K laurate (C_{12}), 5 to K myristate (C_{14}), 6 to K palmitate (C_{16}) and 7 to K stearate (C_{18}).

TABLE 151

Conductivity and Hydrolysis of Sodium Palmitate Solutions

$t = 90°$

c (mol. soap to 1,000 g. H_2O).	λ.	Λ.	Degree of Hydrolysis. Per cent.
0·01	0·001319	137·0	6·6
0·05	0·004210	88·61	2·22
0·1	0·007723	82·51	1·28
0·2	0·01499	82·38	—
0·2996	—	—	0·50
0·347	0·02657	87·04	—
0·5	0·03748	89·48	0·37
0·75	0·05210	87·48	0·30
1·0	0·06263	84·66	0·20
1·5	0·08436	84·50	—

We see from Fig. 119 how the Λ, c curve changes decidedly from lauric acid onwards as compared with the curves of the lower fatty acids; a minimum of Λ appears which is followed by a maximum at higher concentrations.

It was frequently believed earlier that the high conductivity of soap solutions, and perhaps also the departures from normal behaviour, arose from particularly strong hydrolysis. This is however not the case. For as we see from Table 151, the degree of hydrolysis does not reach 7 per cent. even in a $\frac{1}{100}$ molar solution at 90°. The measurements of hydrolysis are thoroughly trustworthy. The electrometric measurement by means of a hydrogen electrode[1] was confirmed to a great extent by means of a catalytic one,[2] which depends upon the catalytic decomposition of the nitrosotriacetonamine being, according to Francis,[3] proportional to the OH' -ion concentration.

The phenomena observed with soap solutions may be largely brought into agreement by assuming with McBain that, in place of the ordinary

[1] *McBain* and *H. E. Martin, loc. cit.* p. 564.
[2] *McBain* and *Bolam, loc. cit.* p. 564.
[3] Journ. Chem. Soc. **101,** 2358 (1912); **103,** 1722 (1913); **107,** 1651 (1915).

fatty acid anions, rapidly migrating micellæ appear, especially in the case of the higher fatty acids and at higher concentrations. The negative constituent of these micellæ is supposed to consist of a large number of fatty acid anions, with which a great deal of fatty acid salt and water is associated; in the case of palmitic acid, the anions of which may be denoted by P′, we might represent the anionic constituent of such a micella by the expression

$$\left[\begin{matrix}(\mathrm{NaP})_m \\ (\mathrm{H_2O})_n\end{matrix}\right] (\mathrm{P}')_r$$

(cf. p. 391); corresponding to the number r of P′ ions the micella carries r charges. The large migration velocity of such a colloid ion should not be arbitrarily assumed, but should agree with the considerations of Stokes and v. Hevesy discussed earlier (cf. p. 393). The ordinary palmitate ion

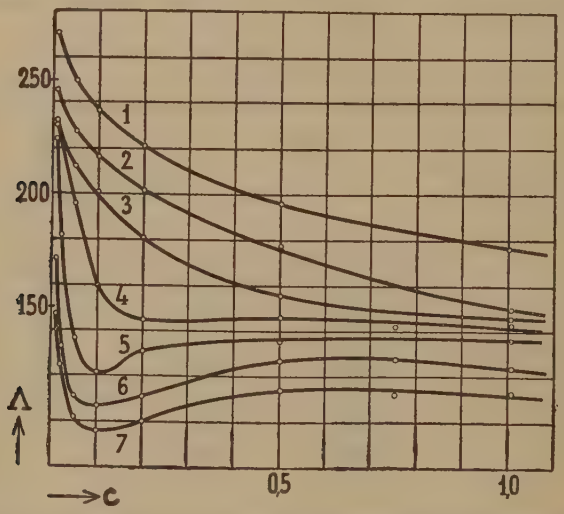


Fig. 119.—Λ, c Curves of the Solutions of Potassium Salts of Fatty Acids.

migrates so slowly (mobility 20·7 at 18°) because the one electron of its charge does not suffice to charge up the large ion to the surface density to which ions tend on the average. With the micella, on the other hand, the ratio of the number of charges to the size is such as corresponds to the rule, and this results in the usual, larger mobility of about 60.

The unusual course of the Λ, c curve is now explained as follows. At small concentrations (particularly with the intermediate acids, such as lauric acid) we have mainly a dissociation of a normal type into alkali kation and fatty acid anion, and the corresponding decrease in Λ with increase in c. At higher concentrations, however, the quickly migrating micellæ are formed in increasing quantities, so that the increase in conductivity thus caused can actually outweigh the decrease caused by diminution in the dissociation. Only at higher concentrations does this decrease again get the upper hand, thus causing the maximum and subsequent decline of Λ.

McBain now compares the osmotic behaviour with the conductivity. It is a further advantage of soap solutions that their large molecular

concentration allows osmotic methods to be used as with true solutions. It is true that strong frothing, and the resulting impossibility of removing air sufficiently completely, renders the boiling-point method uncertain. These difficulties can also hardly be overcome in determining the vapour pressure in a tensimeter. But McBain and Salmon[1] were successful in applying a dew-point method. In this the temperatures were determined at which the water vapour above the soap solution was thrown down as dew upon a highly polished silver surface, or at which this dew disappeared with rise of temperature, as compared with the temperatures at which this happened with pure water. The solution was contained in vessels enclosed in a thermostat of strictly constant temperature. In the vapour space over the solution was hung a cylindrical vessel made of highly polished silver, through which water from another thermostat was pumped. In order to recognize the dew-point, a part of the silver surface was made so wettable that the vapour did not deposit upon it in drops. This was successfully accomplished by previously dipping a part of the silver surface into boiling water. At the dew-point a clear boundary between the two parts of the silver surface was recognizable. By means of this method the depression of the vapour pressure could also be determined at temperatures at which the conductivity measurements had been carried out. Measurements of this kind were supported by very careful freezing-point determinations.

The osmotic behaviour is such as to lead to the calculation of much too small an ionic concentration; the observed conductivity could not therefore be explained from it assuming the ordinary mobilities. If however we assume rapidly migrating micellæ, the osmotic behaviour may be reasonably connected with the results of conductivity measurements. While with K acetate the depression of the freezing-point, in correspondence with the high degree of dissociation, almost amounts to twice the normal—van't Hoff's factor i almost equal to 2—this is already with potassium octoate only the case in dilute solution. At higher concentrations the depression in the freezing-point greatly diminishes. With potassium laurate, and still more so with the actual soaps, the depression in the freezing-point is smaller even at low concentrations than one would calculate assuming correct molecular weight and complete absence of dissociation. The dew-point experiments led to the same result.

By a comparison of conductivity and osmotic measurements McBain was able to calculate approximately the content of different kinds of molecules in the soap solutions. If we assume that in the osmotic measurements the effect of the micellæ, both of non-dissociated and of colloid ions, is small compared with that of molecules and ions, the freezing-point depression gives the total concentration a of alkali kation + fatty acid anion + non-dissociated non-colloidal fatty acid salt. If, in the conductivity, we neglect that of the slowly migrating fatty acid anion as compared with that of the rapidly migrating micella ion—the mobility of which McBain puts equal to that of the $K^{\cdot}$ ion—we get a degree of dissociation from which the amount b of the alkali kation associated with the micellæ can be calculated. If b is subtracted from a, we get substantially the concentration c of the crystalloid constituents of the solution, excluding the alkali kations, and hence the concentration fatty acid anion + non-dissociated non-colloid salt. The difference between c and the total amount

[1] *McBain* and *Salmon*, Proc. Roy. Soc. **97**, A, 44 (1920); Journ. Amer. Chem. Soc. **42**, 426 (1920); see also *Cummings*, Journ. Chem. Soc. **95**, 1772 (1909).

d of fatty acid leads to the fatty acid present as colloid (negatively charged micellæ ions + micellæ of non-dissociated salt). How dissociated and undissociated micellæ are distributed in the total colloid cannot yet be determined with certainty; a certain limit is given by the fact that the total number of fatty acid molecules present in the dissociated micella cannot be larger than the number of the alkali kations. Their content was also confirmed directly by using potential measurements on alkaline amalgams.[1] McBain[2] thus sets limits to the various constituents of the solutions of fatty acid salts, whereby we get at least an approximate picture of the composition of these solutions. In Table 152, together with the values for potassium oleate, a true soap, are given those for potassium laurate, in which the presence of colloidally dissolved molecules begins to become distinct.

TABLE 152

Composition of the Solutions of Fatty Acid Salts at 0–18°

c (mol to 1,000 g. H_2O).	Neutral Colloid $\overline{\lvert (KF)m \rvert}$ $\overline{\lvert (H_2O)n \rvert}$	Colloid Ion $\overline{\lvert (KF)m \rvert}$ $\overline{\lvert (H_2O)n \rvert}(F')_r$	Undissociated Non-colloid Salt KF.	Fatty Acid Anion F′.	Alkali Kation. K′.
		Solution of Potassium Laurate			
0·1	0·01–0·04	0·03–0·00	0·06–0·03	0·00–0·03	0·03
0·2	0·06–0·13	0·07–0·00	0·07–0·01	0·00–0·07	0·07
0·4	0·24–0·26	0·14–0·11	0·03–0·00	0·00–0·03	0·14
0·5	0·30–0·32	0·18–0·16	0·02–0·00	0·00–0·02	0·18
0·6	0·36–0·39	0·21–0·18	0·03–0·00	0·00–0·03	0·21
1·0	0·60–0·64	0·36–0·32	0·04–0·00	0·00–0·04	0·36
2·0	1·21–1·34	0·66–0·53	0·13–0·07	0·00–0·06	0·66
		Solution of Potassium Oleate			
0·1	0·05–0·08	0·02–0·00	0·02–0·00	0·00–0·02	0·02
0·2	0·14–0·15	0·05–0·04	0·01–0·00	0·00–0·01	0·05
0·4	0·28–0·29	0·11	0·00	0·00	0·11
0·5	0·35–0·36	0·14	0·00	0·00	0·14
0·6	0·41–0·43	0·17–0·16	0·01–0·00	0·00–0·01	0·17

The dependence of the osmotic effects upon the temperature are such as indicate much larger colloid concentrations and a higher hydration at low than at high temperatures. This explains the high temperature coefficient of the conductivity shown by soap solutions.

The fatty acid split off hydrolytically in soap solutions is in the case of the higher members so difficultly soluble, that it certainly remains suspended as second phase, but doubtless not alone by itself in a pure state, but united with the colloidal soap micellæ; for solid phases separate from soap solutions, which are to be regarded as mixtures or adsorption compounds of fatty acids and fatty acid salts.[3]

As already remarked, it will probably be possible to apply the point of view here developed for soap solutions to many other hydrophilic colloids,

[1] *Salmon*, Journ. Chem. Soc. **117**, 530 (1920).
[2] *McBain*, Miss *Laing* and *Titley*, *loc. cit.* p. 564.
[3] *Donnan* and *J. S. White*, Journ. Chem. Soc. **99**, 1668 (1911).

particularly to solutions of dyes, proteins, gelatines, etc. There also high conductivities are met with, which change quite regularly and frequently reversibly with the concentration of colloid and added electrolyte. How far one can reckon with relations which correspond more to those in true electrolyte solutions, how far we have to take into account rapidly migrating colloid ions, must be tested from case to case. With solutions of sodium cetylsulphonate, $C_{16}H_{33}SO_3Na$, a substance whose solutions are largely similar to the soaps, Reychler [1] has also determined a similarity in the behaviour of the conductivity and other properties with that of soap solutions.

The relationships are very varied in the case of the proteins. That here also large, rapidly migrating colloid ions can occur, follows from Hardy's [2] experiments, according to which, in very turbid solutions of globulin acetate, the migrating particles of globulin had a velocity of 2 to 3×10^{-4} cm. This velocity was measured by a method due to Whetham.[3]

A case which, after the investigations of Laqueur and Sackur,[4] Brailsford Robertson,[5] and Pauli,[6] may be regarded as very largely elucidated, is that of the solution of casein salts. Casein is very difficultly soluble in water; water, shaken with casein, and poured through a filter, reacts neutral. Nevertheless its acid character may be recognized from the fact that grains of casein, when placed on moist blue litmus paper, produce red spots. In aqueous alkali it dissolves, and the solutions are comparatively clear when the alkali content is high, while upon addition of acid they become more turbid.

The above-named investigators believed that they were justified in applying to these solutions the laws applying to the conductivity of ordinary electrolyte solutions, and Pauli concluded from measurements of this kind that one could entirely explain the behaviour of these solutions by assuming the presence of simple tervalent casein anions and of such associated with a further molecule of casein. These conclusions appear to be doubtful according to the results of Mandoki and Polanyi,[7] who found that although such solutions do not diffuse through parchment, substances which greatly increase the conductivity of the external liquid pass from them through fish bladders. It is not simply a matter of the diffusion of casein salt, for the conductivity calculated upon the same amount of nitrogen is several times greater in the external than in the internal solution. Mandoki and Polanyi suppose that it is due to the decomposition products of the casein, which in their opinion is, like many proteins, very unstable towards alkali; the long shaking with alkali during the preparation of the solutions suffices to decompose it considerably. The observed conductivity would thus

[1] Kolloidzeitschr. **12,** 279 *et seq.* (1913); Bull. soc. chim. d. Belge. **27,** 110, 113 (1913).

[2] Journ. of Physiol. **33,** 291 (1905).

[3] Phil. Trans. **184,** 337 (1893).

[4] *Sackur,* Zeitschr. f. physik. Chemie, **41,** 672 (1902); *Laqueur* and *Sackur,* Beitr. z. Chem. Physiol. u. Pathol. **3,** 193 (1903).

[5] Journ. Phys. Chem. **11,** 542 (1907); **12,** 473 (1908); **13,** 469 (1909); **14,** 528, 601 (1910); **15,** 178 (1911); Journ. biolog. Chem. **2,** 317 (1907); **5,** 147 (1908); *Brailsford Robertson* and *C. L. A. Schmidt, ibid.* **5,** 31 (1908); *Brailsford Robertson* and *Burnett, ibid.* **6,** 105 (1909); *Brailsford Robertson,* "Die physikalische Chemie der Proteine," Dresden, 1912, p. 150 *et seq.*

[6] *Pauli,* Biochem. Zeitschr. **70,** 489 (1915); *Pauli* and *Matula, ibid.* **99,** 219 (1919); *Pauli,* "Kolloidchemie d. Eiweiss Körper," Dresden, 1920, p. 81 *et seq.*

[7] Biochem. Zeitschr. **104,** 254 (1920).

allow no conclusions to be drawn concerning the casein itself, since it arises largely from the products of decomposition.

I should like, in principle, to take similar difficulties into account in the case of other proteins. Hence the results obtained on the basis of conductivity and determination of ionic concentration cannot yet be regarded as generally certain.

In view of the presence of so many comparatively small micellæ as must be assumed in the hydrophilic sols, the distinction between electrolytic and kataphoretic migration becomes artificial. One is, however, tempted to speak of kataphoresis when the sol is as electrolyte-free as possible and the micellæ are to be regarded as fairly large. Also, in the case of hydrophilic sols, the micellæ are generally found to be negatively charged towards water, e.g. in the sols of silicic acid,[1] albumin (as electrolyte-free as possible),[2] starch,[3] etc.; a very strong starch sol containing perceptibly only amylose, and not the negatively charged amylopectin (see p. 635), shows practically no kataphoresis. With the sols of the proteins, gelatine, etc., the decidedly amphoteric nature of the substances comes into play; the kataphoresis shows itself very sensitive to small concentrations of $H^{\cdot}$ and OH' ions, and by changing them a reversal of the charge of the micellæ can be attained with an ease not known with the micellæ of hydrophobic sols.

The Isoelectric Point of Protein Sols

The amphoteric nature of the proteins, gelatines, etc., just referred to, leads to a behaviour of their sols under the influence of the electric current which even without a more exact knowledge of the chemical composition of the colloid ions and their concentration is well and strikingly defined. Thereby, the changes produced in the solution by the experiment are so small, the interference with the conditions so slight, that the considerations just put forward (p. 569) concerning possible considerable changes in the protein molecule may be set aside in this case. In a protein sol, as pure as possible, colloid ions are not originally present in considerable amount; they are formed when acids or alkalis are added; with excess of $H^{\cdot}$ ion we have by preference protein kations, with excess of OH' ion protein anions. There is an intermediate $H^{\cdot}$ or $OH^{\cdot}$ ion concentration at which protein kations and anions are present in equal numbers, which number corresponds to the minimum concentration of protein ions. This special minimum concentration is called by L. Michaelis,[4] who has elucidated these phenomena to a great extent, the *isoelectric point* of the protein in question. It can be determined by means of the electrical transport of the protein in solutions of gradated $H^{\cdot}$ and OH' ion concentration—mixtures of acetic acid and sodium acetate. A middle vessel contains the protein in a solution of given $H^{\cdot}$ ion concentration; right and left are vessels which contain the same acetic acid and sodium acetate mixture, but no protein;

[1] *Whitney* and *Blake*, Journ. Amer. Chem. Soc. **26,** 1374 and 1380 (1904).

[2] *Pauli* and *Handovsky*, Biochem. Zeitschr. **18,** 356 (1909) [cf. also *Pauli*, Beitr. z. chem. Physiol. u. Pathol. **7,** 531 (1906)]; *L. Michaelis*, Biochem. Zeitschr. **19,** 181 (1909).

[3] *Samec* and *v. Hoefft*, Kolloidchem. Beiheft. **5,** 192 *et seq.* (1913).

[4] *L. Michaelis* and *Mostynski*, Biochem. Zeitschr. **24,** 79 (1910); *L. Michaelis* and *Rona*, *ibid.* **27,** 38 (1910); **28,** 193 (1910). *L. Michaelis* and *H. Davidsohn*, *ibid.* **30,** 143 (1910); **33,** 456 (1911); *L. Michaelis*, *ibid.* **33,** 182 (1911); **47,** 250 (1912); *Nernst*-Festschrift, p. 308 (1912). Concerning the theory of the isoelectric point see also *Sörensen*, Zeitschr. f. physiol. Chemie, **103,** 192 *et seq.* (1918).

into these dip the reversible electrodes. If protein kations are preferentially formed, the protein migrates to the negative pole; and to the positive, if anions are preferentially formed. At the isoelectric point the least migration of the protein is observed. Table 153 gives a picture of this behaviour.

TABLE 153

Kataphoresis of Natural Ox Serum Albumin at different H· Ion Concentrations[1]

Albumin Content ca. 0·1%. Na Acetate 0·02 N.

(Acetic acid) (Sod. acetate).	H· ion Concentration (measured with Gas Electrode).	Direction of Migration.
6 : 1	$0{\cdot}12 \cdot 10^{-3}$	To cathode
4 : 1	$0{\cdot}85 \cdot 10^{-4}$	„
2 : 1	$0{\cdot}38 \cdot 10^{-4}$	„
1 : 1	$0{\cdot}20 \cdot 10^{-4}$	Anode and cathode; cathode stronger
1 : 2	$0{\cdot}11 \cdot 10^{-4}$	To cathode
1 : 2	$0{\cdot}10 \cdot 10^{-4}$	To anode
1 : 4	$0{\cdot}49 \cdot 10^{-5}$	„
1 : 6	$0{\cdot}45 \cdot 10^{-5}$	„
1 : 8	$0{\cdot}19 \cdot 10^{-5}$	„

Michaelis assumes that equilibria exist between the protein ions and the undissociated protein micellæ, just as are known between smaller ions, and experience with soap solutions causes this assumption to appear entirely legitimate. If the undissociated protein molecule is represented by HROH, it then dissociates, in the first place, as an acid according to the equation

$$K_a = \frac{(ROH') \cdot (H')}{(HROH)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and then as base according to the equation ,

$$K_b = \frac{(HR') \cdot (OH')}{(HROH)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here K_a and K_b are the strengths of the acid and the base. The brackets denote concentrations. It may easily be deduced from equations (1) and (2), according to the theory of amphoteric electrolytes,[2] that, for that concentration of acid at which the concentration of the protein kations is equal to that of the anions, that is at the isoelectric point, the H· ion concentration, y, is given by the equation

$$y = \sqrt{\frac{K_a}{K_b} K_w} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where K_w is the ionic product of water.

[1] *Michaelis* and *Davidsohn*, Biochem. Zeitschr. **33**, 456 (1911).

[2] *Bredig*, Zeitschr. f. Elektrochem. **6**, 33 (1899); Ber. d. deutsch. chem. Ges. **37**, 4140 (1904); *Winkelblech*, Zeitschr. f. physik. Chemie, **36**, 546 (1901); see particularly *Lundén*, "Affinitätsmessungen der schwachen Säuren und Basen," Sammlung chem. u. chem.-techn. Vorträge **14** (1908), p. 49 *et seq.*

From equation (3) $\frac{K_a}{K_b}$, the ratio of the acid and basic strengths of the protein may be found. The values thus found agree entirely with the behaviour in other respects of the proteins in question. Casein, for example, has a distinctly acid character; the casein grains, which are practically insoluble in water, become red, as mentioned on p. 569, when in contact with moist litmus paper. To this fact corresponds a fairly large value of $y = 2 \times 10^{-5}$, from which $\frac{K_a}{K_b} = 5 \times 10^{-4}$ would result. Regarding a few more isoelectric points of proteins, see p. 574.

Now it is still questionable, as follows from later considerations (cf. p. 609), whether this behaviour of the proteins may really be definitely explained in the manner assumed here. This view presupposes that the isoelectric point is a function of the $H^{\cdot}$ and OH' ion concentrations alone, and is independent of other kinds of ions; this, however, does not appear to be unconditionally true.[1] On the contrary, an influence of other ions, of a kind similar to that met with most distinctly during the flocculation of hydrophobic sols, becomes noticeable.

If this objection is set aside for the present, then unmistakably the isoelectric point is also apparent in respect of other properties of protein sols. As already mentioned (p. 543), the production of the protein ions upon addition of alkali or acid causes a strong increase in viscosity. According to this it must be at a minimum at the isoelectric point, since a minimum of the protein ion concentration lies there. This is the case.[2] The optical rotation also shows a minimum, since the protein ions rotate more strongly than the undissociated protein micellæ.[3] The isoelectric point is also of influence in the Donnan membrane equilibrium. Rona and György[4] dialysed serum, the $H^{\cdot}$ ion concentration of which had been altered by addition of acetic acid, against pure water, and determined after long-continued dialysis the $H^{\cdot}$ and Cl' ion content of the serum. It was found that above a $H^{\cdot}$ ion concentration of $1{\cdot}5 \times 10^{-5}$, when therefore increasingly more protein kations were present, the Cl' ion concentration in the internal liquid was greater than in the external; below $1{\cdot}5 \times 10^{-5}$, when the protein anions preponderated, there was, conversely, less Cl' ion in the internal than in the external liquid. The isoelectric points of serum-albumin and serum-globulin lie in the range from 10^{-5} to 10^{-6}. It is naturally entirely in agreement with the Donnan theory that colloid kations prevent the in-diffusion of the kations, and colloid anions that of the anions. The connexion between the isoelectric point and the conditions of stability of the protein sols will be discussed later (p. 573).[5]

[1] *L. Michaelis* and *Rona*, Biochem. Zeitschr. **94,** 225 (1919).

[2] *Pauli* and *Matula*, Kolloidzeitschr. **12,** 222 (1913). It deserves remark, that even with hydrophilic sols of non-amphoteric substances, e.g. with soap solutions, the viscosity not far from the neutral point passes through a minimum [see *Mayer, Schaeffer,* and *Terroine*, Compt. rendu, **146,** 484 (1908), and *Farrow*, Journ. Chem. Soc. **101,** 347 (1912)].

[3] *Pauli* and *Samec*, Biochem. Zeitschr. **59,** 470 (1914).

[4] Biochem. Zeitschr. **56,** 431 (1913).

[5] The salts of many amphoteric substances, e.g. casein [cf. *Berczeller*, Biochem. Zeitschr. **53,** 232 (1913)] lower the surface tension strongly, whilst the neutral micellæ are only slightly capillary-active,—a remarkable deviation from the normal behaviour, according to which salts are less capillary-active than the acids and bases.

The Stability of Lyophilic Sols. "Salting Out."

In the stability of lyophilic sols influences act across one another in a manner often difficult to penetrate; influences such as are known from the case of true solutions, and such as are met with in the case of hydrophobic sols.

The hydrophilic sols are also so varied that it is at present difficult to say anything in general about their conditions of stability. As regards details this must be postponed until the Special Part. In the following section only a few striking and distinctive processes will be discussed, in particular those in which decided differences exist as compared with hydrophobic sols.

It is never necessary to take into account a settlement of the micellæ in consequence of a sedimentation equilibrium, as in the case of Perrin's experiments on gamboge particles (see p. 343). With a large number of lyophilic sols, molecular weights up to a few 100,000 may be assumed; with one of 50,000, a density a little above 1, and at room temperature the concentration of the sol would, even at a height of 10 metres, only have declined by $\frac{1}{10}$. If we consider that the difference in density between micella and intermicellar liquid is usually slight, and the degree of dispersion great, the rate of fall will be small. Evidently, therefore, it is unnecessary, in practice, to take into account an influence of gravity upon the stability of lyophilic sols.

The striking difference between hydrophilic and hydrophobic sols is the difference frequently referred to between their stability towards electrolytes, which indeed is the main reason for separating them into two groups. When one sees what considerable concentrations of acids and alkalis, alkali and alkaline-earth salts can be added to sols of silicic acid, proteins, gelatines, starch, and so on, without sensibly affecting the stability of the sols, one might at first believe in an absolutely fundamental difference. Upon closer examination this impression disappears, and unmistakable similarities with the behaviour of hydrophobic sols come to light. This is not only true of sols such as those of sulphur and others, in the case of which one is in doubt in which group they should actually be placed. Even with unquestionably hydrophilic sols such similarities appear.

Thus Michaelis [1] found that with sols of amphoteric substances, such as the proteins, etc., a minimum of stability exists, as in the case of hydrophobic sols, at the isoelectric point—as found from kataphoresis. If therefore electrolyte mixtures of graded $H^{\cdot}$ ion concentration are added to protein sols, the greatest precipitation is observed in many cases when the $H^{\cdot}$ ion concentration corresponds to the isoelectric point. The following table shows how good is the agreement. The determination of the optimum of precipitation is a second method of determining the isoelectric point.

But it is questionable how far it is permissible to explain this phenomenon in the same way as for hydrophobic sols, namely, that the discharged particles can adhere well to one another (cf. p. 416), for it appears that this behaviour is not general. Natural (not denatured) serum albumin and hæmoglobin give an isoelectric point as determined by the electrical transport (cf. Table 154). They are not however flocculated at this point. If we attempt to explain this by the particularly small size of the particles, we can see no reason why sufficiently large particles should not finally be

[1] *loc. cit.* p. 570.

TABLE 154

Optimum of Precipitation and Isoelectric Point of Proteins

Protein.	Isoelectric Point determined.	
	By Kataphoresis.	As Optimum of Precipitation.
Natural serum albumin [1]	2×10^{-5}	—
Denatured serum abumin [2]	about 4×10^{-6}	$3{\cdot}8 \times 10^{-6}$
Serum globulin [3]	about 4×10^{-6}	$3{\cdot}8 \times 10^{-6}$
Casein [3]	2×10^{-5}	2×10^{-5}
Oxyhæmoglobin [4]	$1{\cdot}8 \times 10^{-7}$	—
Trypsin [5] (pancreasnucleoprotein)	3×10^{-4}	3×10^{-4}
Gelatine [6]	2×10^{-5}	—

formed, if the micellæ on colliding remain adhering to one another. One will therefore consider the other possible explanation, that the undissociated protein present in the largest concentration at the isoelectric point is particularly difficultly soluble, and hence separates out. It is well known that the less dissociated acids and bases are generally more difficultly soluble than the strongly dissociated salts. This connexion is strikingly demonstrated by an experiment of L. Michaelis and H. Davidsohn,[7] according to which the amphoteric *p*-aminobenzoic acid also crystallizes out readily and freely at the isoelectric point, while with excess of H· and OH′ ions it remains in solution, since the free acid is more difficultly soluble than its salts.

Now in actual fact much tells in favour of regarding the separation of the disperse phase of hydrophilic sols as the precipitation of a difficultly soluble substance, for the solubility of which the requirements of the Gibbs phase rule would then be fulfilled to a large extent. This is the case, for example, for the *salting out* of the proteins, gelatines and other similar colloidally dissolved substances.[8] They separate at large concentrations of alkali salts (several times molar) as a second phase, generally in amorphous flakes; in individual cases, in which the colloidally dissolved substance may be regarded to a large extent as chemically homogeneous, also in crystalline form. The process is reversible; by dilution of the solution the separated matter can be redissolved.

Sörensen [9] has investigated closely the separation of egg albumin in crystalline form from ammonium sulphate solution. If it is a question of true solubility, the solution should have the same albumin content after

[1] *L. Michaelis* and *H. Davidsohn*, Biochem. Zeitschr. **33**, 456 (1911).
[2] *L. Michaelis* and *Rona*, Biochem. Zeitschr. **27**, 38 (1910).
[3] *Rona* and *L. Michaelis*, *ibid.* **28**, 193 (1910).
[4] *L. Michaelis* and *Takahashi*, *ibid.* **29**, 439 (1910).
[5] *L. Michaelis* and *H. Davidsohn*, *ibid.* **30**, 481 (1911).
[6] *L. Michaelis*, *Nernst*-Festschrift, p. 318 (1912).
[7] Biochem. Zeitschr. **30**, 143 (1910).
[8] This view was first upheld by *Spiro* [Beitr. z. Chem. Physiol. u. Pathol. **4**, 300 (1903)] and *Galeotti* [Zeitschr. f. physiol. Chemie, **44**, 461 (1905); **48**, 473 (1906); *Guerrini*, *ibid.* **47**, 287 (1906); *Scaffidi*, *ibid.* **55**, 42 (1907)].
[9] *Sörensen* and Frl. *Höyrup*, Zeitschr. f. physiol. Chemie, **103**, 211; 267 (1918).

precipitation independently of the original albumin content, provided that the composition of the solution in respect of ammonium sulphate is also the same. This was sensibly the case; the content of the sols investigated lay, at the commencement, between 2·350 and 14·140 g. of hydrated albumin to 100 g. of water in the solution, while the solutions in equilibrium with the separated albumin contained after 16 days between 0·597 and 0·768 g. of hydrated albumin to 100 g. of water. Since the albumin which separates takes a great deal of water with it—0·22 g. water to 1 g. dry albumin—great care had to be taken that the $(NH_4)_2SO_4$ content of the equilibrium solution was not thereby changed; that is to say, the $(NH_4)_2SO_4$ content had to be so chosen originally that it remained the same in the equilibrium solution, when the particular amount of water was removed from the solution by the albumin. Discrepant results such as those, for example, observed by Miss Chick and C. J. Martin,[1] for the separation of amorphous ovalbumin from ammonium sulphate solution—greater separation from a solution originally more concentrated—were explained by Sörensen on the grounds that the ammonium sulphate content was not equally great in the equilibrium solution, but, on the contrary, was larger in the solution in which more albumin had separated, and that a larger $(NH_4)_2SO_4$ content corresponds to a smaller solubility.

It is true that the regularities do not by any means agree so closely, as may already be seen from the figures given, as is usual with phase equilibrium in the case of truly dissolved substances. Indeed, phenomena appear such as are known from the coagulation of hydrophobic sols. Thus, according to experiments by Höber and Gordon,[2] the rate of mixing of an albumin sol and salt solution makes some difference. More is precipitated with rapid than with slow addition; if, for example, 5 c.c. of a 75 per cent. $(NH_4)_2SO_4$ solution are immediately added to 5 c.c. of egg albumin sol, a definite volume of the filtrate contains 0·17 g. albumin; if mixture takes place in the course of 24 or 48 hours, more albumin is found in the filtrate, namely 0·214 and 0·237 g. respectively. A gelatine sol behaves similarly. That which separates is not simply a crystalline substance in equilibrium and definitely characterized, but, at the best, finely crystalline flakes which do not necessarily correspond to an equilibrium and hence settle at different rates and in different amounts according to the conditions of precipitation.

Above all, circumstances which affect adversely the establishment of equilibrium take effect to an extent and degree not the rule in true solutions. In the first place the equilibria are frequently established very slowly; even after a period of 16 days there is no guarantee that the end state is reached. To extend further the time of waiting is, on the other hand, dangerous, since the substances in question, particularly the proteins, are so reactive, that one must expect a sensible change by hydrolysis or by the action of bacteria. Above all, it is again the $H^{\cdot}$ and OH' ion concentrations which can powerfully change the conditions of experiment. Thus Sörensen and Frl. Höyrup [3] found that the rate of separation of egg albumin from ammonium sulphate solutions depends very greatly upon the $H^{\cdot}$ and OH' ion concentration. At a certain $H^{\cdot}$ ion concentration—which on its part is connected with the $(NH_4)_2SO_4$ concentration—we have an optimum velocity, which decreases both with decrease and with increase

[1] Biochem. Journ. **7**, 380 (1913).
[2] Beitr. z. Chem. Physiol. u. Pathol. **5**, 436 (1904), cf. p. 538.
[3] Zeitschr. f. physiol. Chemie, **103**, 267 (1918).

in $H^{\cdot}$ ion concentration. In weakly acid solution the solid phase does not differ sensibly in appearance from the solid which separates at the optimum rate. But even in solutions less acid it loses its crystalline character and becomes amorphous, a sign that it has altered fundamentally. Sörensen rightly emphasizes that even a small contamination of the $(NH_4)_2SO_4$ with H_2SO_4 suffices to displace the observed equilibrium entirely. Hence with these equilibria in lyophilic sols we have to take impurities into account which one does not need to reckon with otherwise in phase equilibria. In the case of these processes and equilibria, which depend so greatly upon the $H^{\cdot}$ ion concentration, it is always necessary to maintain the latter as strictly constant as possible.

In view of these results we shall be cautious in drawing the conclusion that lyophilic sols behave fundamentally differently from true solutions. It is true that there are apparently many cases, such for example as the salting-out of soap solutions [1] (cf. p. 688), in which, as a result of adsorption phenomena, the separation of the solid phase takes place quite differently from the manner required by the phase rule. And the possibility must naturally not be excluded that, as in the case of lyophobic sols, influences due to hydration must secondarily be reckoned with (p. 427), so here electrical influences, variation in the size of the micellæ salted out, and the like, which may cause behaviour such as that described by Höber and Gordon (cf. p. 575), must also be taken into account secondarily.

The conception of the salting-out of the disperse phase of hydrophilic sols as a solubility influence is further confirmed by the fact that the nature of the salt asserts itself entirely in the direction known to us from the effect on the solubility of truly dissolved substances in water.[2] The lyotropic series of anions and kations appears in a pronounced manner. This is seen from Table 155; it is taken from experiments by Hofmeister and his pupils,[3] who were the first to investigate these relations in detail. He determined the lower limit of concentration (molar) at which a sol of white of egg (which still contains the globulin) was immediately rendered turbid. The process is reversible in neutral solution; upon dilution the separated protein redissolves. We have therefore again the series

Citrate > tartrate > sulphate > acetate > chloride > nitrate > chlorate

That iodides and thiocyanates do not produce a turbidity in attainable concentrations corresponds to their position after the nitrates and chlorates. The kation series is less clearly marked.

This behaviour holds for neutral and weakly alkaline solutions. In the latter the corresponding concentration of salt required to produce a turbidity is higher. In weakly acid solutions the series for the salting-out action is, in the case of the anion, reversed, as was first described by Posternak [4] and Pauli.[5] It has already been mentioned (p. 575) that in acid protein solutions the solid phase has become different, for at more

[1] *McBain* and Miss *Taylor, loc. cit.*, p. 564.

[2] Regarding the lyotropic series in the case of the influence on solubility, see particularly the experiments of *Rothmund* on the modification of the solubility of phenylthiourea [Zeitschr. f. physik. Chemie, **33**, 401 (1900); further W. Biltz, *ibid.* **43**, 41 (1903)] and those of *Geffcken* upon the modification of the solubility of difficultly soluble gases [*ibid.* **49**, 257 (1904)].

[3] *Lewith*, Arch. f. experim. Pathol. u. Pharmakol. **24**, 1 (1888); *Hofmeister, ibid.*, **24**, 247 (1888).

[4] Ann. de l'Instit. Pasteur, **15**, 85 (1901).

[5] Beitr. z. chem. Physiol. u. Pathol. **5**, 27 (1904).

TABLE 155

The Salting-out of White of Egg Sol by Alkali and Magnesium Salts in Neutral Solution

$t = 30–40°$

	Li.	K.	Na.	NH_4.	Mg.
Citrate	—	0·56	0·56	—	—
Tartrate	—	0·75	0·78	—	—
Sulphate	0·78	—	0·80	1;00	1·32
Acetate	—	1·67	1·69	—	—
Chloride	—	3·52	3·62	—	—
Nitrate	—	—	5·42	—	—
Chlorate	—	—	5·52	—	—

considerable concentrations of acid (about 0·3 molar) the process is not reversible; the salted-out flakes do not re-peptize on dilution. At smaller acid concentrations the acetates and sulphates still precipitate reversibly, while for example the thiocyanates and iodides give unpeptizable flakes. In order to elucidate this behaviour, experiments of Pauli's are given in the following table in which the change observed immediately after the addition of the electrolyte solution is given.

TABLE 156

The Salting-out of White of Egg Sols by Alkali and Magnesium Salts in Acid Solution[1]

Salt concentration 0·5 N; HCl 0·03 N

	Na.	K.	NH_4.	Mg.
SO_4	Very slight turbidity	Very slight turbidity	Opalescent	Opalescent.
Cl	Slight turbidity	,, ,,	Very slight turbidity	Very slight turbidity
Br	Milky, slight turbidity	Dense, fine turbidity	Fine turbidity	Slight turbidity.
NO_3	Dense milky	Dense milky	Dense milky	Dense milky.
CNS	More densely milky precipitate	More densely milky precipitate	More densely milky precipitate	More densely milky precipitate.

Also in the salting-out (and increase in solubility) of simple amino acids such as leucine and others, the same ionic series is observed, and it varies in the same way when neutral and acid amino acids are compared.[2]

It is true that all these investigations on the influence of the nature of the ions upon salting-out are in so far in need of confirmation, that sufficient care has scarcely ever been taken to keep the $H^{\cdot}$ ion concentration strictly constant in comparing different salts.

[1] *Pauli*, Beitr. z. chem. Physiol. u. Pathol. **5**, 47 (1904).
[2] *P. Pfeiffer* and *Würgler*, Zeitschr. f. physiol. Chemie, **97**, 128 (1916).

It may be remarked here by way of a digression that this influence of the H· and OH′ ion concentration upon the lyotropic series also appears in other processes which are not part of colloid chemistry. Hober [1] pointed out the following. In *acid* catalysis of esters and *acid* inversion of cane sugar bromides favour the reaction more strongly than chlorides, sulphates inhibit it; the series is therefore

$$Br > Cl > SO_4.$$

The order in which the kations accelerate the ester catalysis is, according to Höber,

$$Li > Na > K > Rb > Cs.$$

Conversely, sulphates and thiosulphates, according to Spohr [2] and Arrhenius,[3] assist *basic* saponification of esters, and, according to Koelichen,[4] the *basic* transformation of acetone into diacetone alcohol, while the first reaction is inhibited to an increasing extent by acetates, chlorides, bromides, nitrates and iodides, and the latter by chlorides and nitrates. The series is therefore

$$SO_4 > S_2O_3 > \text{Acetate} > Cl > Br > NO_3 > I.$$

As regards the kations, Höber found for ester hydrolysis the series

$$Cs > Rb > K > Li,$$

Cs inhibiting least and Li most.

From the behaviour described above the following conclusions may be drawn concerning the stability of protein sols and of many other hydrophilic sols. The colloidally dissolved substance has a solubility in water, which is conditioned by a chemical equilibrium between it and the water molecules. The electrolytes cause salting-out since, being themselves hydrated, they displace the equilibria. From known data it is not possible to decide how far it is mainly a matter of the water molecules, which according to the nature of the salt ions are removed from or added to the micella, or of the action of the salts upon the equilibrium between the various polymeric forms of liquid water. Nor is it any more possible to decide how far it is a matter of the ions of the salt entering or leaving the micellæ.

The contrast between the lyotropic series in acid and alkaline solution might be interpreted as follows. If the separation of the micellæ as second phase depends upon water being removed from them, if therefore an equation

$$\text{Colloidally dissolved micellæ} \rightarrow \text{second phase} + nH_2O \quad . \quad . \quad (1)$$

holds, SO'_4 would favour the process most, CNS′ least strongly; we may assume that SO_4' attracts water most strongly, and CNS′ least. The order of the anions would evidently be reversed if, conversely, the second phase separated containing more water than the micellæ, according to an equation

$$\text{Colloidally dissolved micellæ} + nH_2O \rightarrow \text{second phase} \quad . \quad . \quad (2)$$

Substances which bind water strongly would then adversely affect the

[1] Beitr. z. chem. Physiol. u. Pathol. **9**, 35 (1907); Zeitschr. f. physik. Chemie, **70**, 134 (1910).
[2] Zeitschr. f. physik. Chemie, **2**, 194 (1888).
[3] Zeitschr. f. physik. Chemie, **4**, 226 (1889).
[4] Zeitschr. f. physik. Chemie, **33**, 176 (1900).

separation of the second phase, substances binding water slightly would favour it.

Quite similar considerations may be put forward for the chemical reactions just mentioned which are influenced in opposite senses. We know too little concerning the equilibrium between the solution molecules of the reacting substance contained in the water, and the hydration of the ions, to be able to develop these conceptions more exactly.

To test them it would be important to know whether the micellæ of the hydrophilic sols are larger or smaller in presence of the electrolyte than in pure water. This could no doubt be decided by diffusion measurements in presence and absence of the electrolyte. According to Dabrowski [1] egg albumin has a higher diffusion velocity in ammonium sulphate than in pure water. According to this the micellæ were smaller, in agreement with equation (1). According to equation (2) it would be expected that when $H^{\cdot}$ ions are present in addition to the ammonium sulphate, the micellæ would be larger and diffuse more slowly.

Even with the electrocratic sols two cases of coagulation could be distinguished, the one in which the disperse phase separated as flakes, the other in which the whole liquid became more viscous and set to a jelly, as in the case of Al_2O_3 sols. According to present experience both these processes depended in quite the same manner on the nature and concentration of the electrolytes (cf. p. 421). Hence there was no reason for regarding them as essentially different. Nevertheless, a behaviour such as that of an Al_2O_3 sol is only found with sols that are more closely connected with the hydrophilic sols, for which therefore a considerable affinity between micella and solvent must be assumed. Hence a tendency of this kind on the part of a sol to set to a solid jelly, that is, to change into a gel, is more general among hydrophilic than among hydrophobic sols. The *sol-gel transformation* of hydrophilic sols stands in a certain relation to the phenomena of salting-out, but this is certainly not so close that the same explanation can be applied indifferently to either. As the sol-gel transformation requires for its comprehension a more exact knowledge of the nature of gels, it is better not to deal with it here in detail, but in connexion with the behaviour of gels in other respects (cf. p. 700).

The Peptizing Action of Electrolytes on the Micellæ of Hydrophilic Sols

Salting-out occurs at high electrolyte concentrations. At lower ones, on the contrary, a peptizing action of electrolytes is frequently observed. It has been particularly investigated in the case of some proteins or mixtures of proteins, the globulins, in which it is found particularly clearly. The globulins are present in many naturally occurring protein solutions only because the concentration of electrolyte suffices to peptize them. If the electrolytes are removed from the solution by dialysis, the globulins separate out, since they only remain in solution in the neighbourhood of their isoelectric point when sufficient amounts of peptizing electrolyte are present.

Miss Chick [2] has followed the peptizing action of various electrolytes upon the globulin of horse serum. In this connexion two processes can

[1] *loc. cit.* p. 556.
[2] Biochem. Journ. **7**, 318 (1913).

unmistakably be distinguished. In the first place, anions and kations of high valency such as citrate and $La^{\cdots}$ ions play a prominent part (see Table 157); they charge the particles, the citrate ion negatively, and the

TABLE 157

Coagulation and Peptization of a Globulin by Electrolytes

Concentration of globulin solution, 0·016 per cent.

Electrolyte.	Concentration of Electrolyte Solution in Normality.	Degree of Coagulation or Peptization.	Electric Charge.
NaCl . .	0·01	Complete coagulation	
	0·02	,, ,,	
	0·03	Not quite complete coagulation	
	0·04	,, ,, ,,	
	0·045	,, ,, ,,	Negative (the coagulated particles)
	0·05	Partial coagulation	,, ,,
Na_2SO_4 .	0·0005	Complete coagulation	
	0·001	,, ,,	
	0·01	,, ,,	
	0·02	Not quite complete coagulation	,, ,,
	0·03	Partial coagulation	
	0·04	Almost complete peptization	,, ,,
	0·05	Complete peptization, clear solution	
Na_3 citrate	0·0005	Partial coagulation	Negative.
	0·001	,, ,,	
	0·002	Almost complete peptization	
	0·003	Complete peptization, clear solution	
$BaCl_2$.	0·001	Complete coagulation	
	0·005	Not quite complete coagulation	
	0·01	,, ,, ,,	No migration
	0·02	Partial coagulation	,, ,,
	0·03	Almost complete peptization	
	0·05	Complete peptization, clear solution	,, ,,
$La(NO_3)_3$	0·001	Not quite complete coagulation	Positive
	0·005	,, ,, ,,	
	0·006	Almost complete peptization	Positive
	0·01	,, ,, ,,	
	0·02	Complete peptization, clear solution	

$La^{\cdots}$ ion positively, as may be deduced from the kataphoretic migration of the micellæ. This is evidently the same charging and peptizing action of strongly adsorbable ions of high valency which was described for the hydrophobic sols, and which causes the irregular series (cf. p. 430). The ultramicroscopic appearance agrees with this; one sees fairly equally sized and uniformly distributed micellæ, which are continually divided up more finely with increase in electrolyte concentration.

But in addition to this another influence is present. It appears at high concentrations of the salts with but slightly active ions, but also at high concentrations of those with active ions, such as the citrate or $La^{\cdots}$ ion.

The globulin particles peptized under these conditions do not migrate with the current; they appear uncharged. This peptization may be distinguished from the *electrical* as *neutral*. The ultramicroscopic picture is also different; we have an optically empty solution along with coarser unpeptized residues of the globulin, which become the smaller the stronger the electrolyte solution.

If for the present we take no account of the fact that we are dealing with peptizations arising from different causes, it is again remarkable that the valency of the anions is altogether not unimportant for the peptization. If only alkali salts are compared, then with the Cl′ ion peptization is not reached, with the SO_4'' ion it appears at an appreciably higher concentration than with the citrate ion. Hardy [1] explains this dissolution on the basis of the formation of a compound of the protein with the salts, in which he supposes both anions and kations of the salt to be associated with the nitrogen of the ammonium group. Pfeiffer [2] considers the formation of a compound according to the equation

$$R\begin{matrix}NH_2\\COOH\end{matrix} + NaCl = R\begin{matrix}Cl\\NH_3\\COONa\end{matrix} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

as more probable. He and his co-workers were able to prepare such compounds of protein and salt even in crystalline form, and the increase in the solubility of compounds of simple amino-acids such as glycine and others followed rules quite similar to those for the proteins. On the other hand, Schryver [3] would like rather to regard it as an adsorption of the salts named upon the protein micellæ; this might hinder the association of the micellæ with simultaneous dehydration; and as such he regards the separation of globulin in solutions poor in electrolytes (cf. equation (1) p. 578). Whether it is a matter, in the case of the proteins, of a straightforward interaction according to equation (1), is perhaps questionable. It is possible that this view is opposed by the statement that with equal concentrations of electrolyte the more globulin peptized neutrally, the more concentrated was the original globulin solution.[4] This might be explained, according to Miss Chick,[5] as follows. The more concentrated the original globulin solution, the more extensive is the interface of the separated globulin flakes, the greater is the adsorption of electrolyte—or also its chemical interaction—and the stronger is the peptizing action.

That the globulin micellæ bind electrolyte follows from the fact that the conductivity of the electrolyte solution is reduced by addition of globulin,[6] and, indeed, comparatively more strongly in the case of electrical than of neutral peptization. At higher electrolyte concentrations the globulin sol is salted out.

[1] Journ. of Physiol. **33**, 251 (1905).

[2] *P. Pfeiffer* and *v. Modelski*, Zeitschr. f. physiol. Chemie, **81**, 331 (1912); **85**, 1 (1915); *P. Pfeiffer* and *Wittka*, Ber. d. deutsch. chem. Ges. **48**, 1289 (1915); *P. Pfeiffer, ibid.* **49**, 1938 (1915); *P. Pfeiffer* and *Würgler*, Zeitschr. f. physiol. Chemie, **97**, 128 (1916).

[3] Proc. Roy. Soc. **83**, B, 96 (1910).

[4] *Mellanby*, Journ. of Physiol. **33**, 338 (1905); *Hardy, loc. cit.* under [1].

[5] Biochem. Journ. **7**, 331 (1913).

[6] *Hardy, loc. cit.* under [1]; Miss Chick, *loc. cit.* p. 579.

Influence of Temperature Changes upon the Stability of Hydrophilic Sols

The influence exerted by a rise of temperature upon the stability of hydrophilic sols can hardly be definitely described; we are too often dealing with chemical interactions between the micella and the dispersion medium, as in the denaturing of proteins (cf. p. 611), to be able to set up a general rule. Perhaps it may be said that if we leave aside special chemical interactions, a considerable increase in peptization is usually effected by increase of temperature, corresponding with the frequently observed rise of solubility with temperature.

It is more possible to say something by way of summary concerning the influence of freezing,[1] for the fact that hydrophilic sols are more easily peptized than hydrophobic is usually of influence. Upon freezing we observe, as with the latter, that the micellæ are forced together by the ice in crystallizing out, and finally separate in the form of flakes or (with e.g. gelatine) of a fine network with many meshes. The micellæ of many sols, such as gum tragacanth, hæmoglobin, re-peptize easily by simple thawing and warming to ordinary temperature. Others, such as gelatine and starch, must be appreciably warmed together with the dispersion medium in order that they may again pass into colloidal solution. The circumstance thus makes itself felt that the gel separated is also simultaneously dehydrated. Hence the same influences which will be of importance later (p. 662) in connexion with the taking-up of water by dried gels come into consideration. The difference between hydrophobic and hydrophilic sols also appears clearly in the following fact. The ordinary unprotected metallic sols cannot be re-peptized by thawing; protected metallic sols, on the other hand, which therefore contain hydrophilic colloids, go again into solution, more or less smoothly, upon thawing.

Since the micellæ of hydrophilic sols often allow themselves to be re-peptized by simple warming with the dispersion medium, they may be purified by freezing out and separation of the liquid after thawing.[2]

The Interaction between Hydrophilic and Hydrophobic Sols

Hydrophilic and hydrophobic sols influence one another's stability in extremely varied ways, which are all the more difficult to penetrate, as foreign electrolytes, often in very small concentrations, are of decisive influence, and a slight change in the proportionate amounts of the disperse phases of the interacting sols fundamentally alters the observed behaviour. In some limiting cases the observed phenomena seem to have been successfully interpreted. It is therefore preferable to consider these cases more closely and to assume that more complicated cases can be referred to these fundamental phenomena.

The Flocculation of Hydrophobic by Hydrophilic Sols

If a hydrophilic sol, e.g. a gelatine solution as free as possible from electrolytes, is added in small concentration to a negative hydrophobic

[1] See *H. W. Fischer*, Beitr. z. Biologie d. Pflanzen (1910), p. 133; *H. W. Fischer*, and *Bobertag*, Biochem. Zeitschr. **18**, 58 (1909).

[2] See *Malfitano* and Mdlle. *Moschkoff*, Compt. rendu, **150**, 710 (1910); **151**, 817 (1910).

sol, such as, say, a faintly acid Donau gold sol or a Carey Lea silver sol, the hydrophobic sol is coagulated; the red gold sol changes to blue, the greenish brown silver sol first turns black and then allows the flakes to fall.

It is not necessary for flocculation to occur. The charge of the micellæ of the hydrophobic sol and the concentration relations may be such that this does not happen. But a change has none the less taken place in the direction of a diminution in stability. With silver sols the colour has changed towards black, and the concentration of an electrolyte required to flocculate is found to be smaller than with the pure gelatine-free silver sol. This phenomenon, that a hydrophilic sol does not directly flocculate a hydrophobic sol, but does decrease its stability, has been given a special name and been described as the *sensitization* of the hydrophobic by the hydrophilic sol.

A sensitization of this kind, probably depending upon the same cause, has been observed in the case of Fe_2O_3 sols. If an albumin sol purified by dialysis is added to a Fe_2O_3 sol also thus purified, a Fe_2O_3-albumin sol is obtained, which differs externally but little from the pure aqueous Fe_2O_3 sol. In the investigation of Brossa and Freundlich,[1] to which particular reference is made, a serum albumin solution dialysed for three weeks and freed from globulin was used. The Fe_2O_3-albumin sol is a little more turbid than the original pure aqueous Fe_2O_3 sol, but cannot be any more resolved in the ultramicroscope than the latter; but it differs by frothing strongly on shaking. Under the conditions here considered the Fe_2O_3 appears to be present in excess. That does not mean to say that it must needs be in excess by weight; what matters is rather the unknown large number of Fe_2O_3 micellæ, which behave as adsorbent towards the albumin, which distributes itself between them and the intermicellar liquid. Upon what the sensitization depends now becomes clear from the kataphoretic migration velocity.

The Fe_2O_3-albumin sol migrates, as does the pure aqueous Fe_2O_3 sol, to the negative pole; the micellæ are therefore positively charged. Their migration velocity is, however, considerably smaller than that of the micellæ of the pure aqueous sol. According to equation (8), p. 244, their charge is therefore correspondingly smaller. According to the theory of the flocculation of hydrophobic sols (cf. p. 418), a much smaller concentration of the active ion is necessary with a small charge on the particle; from this follows the sensitization. The same depression of the kataphoretic migration velocity was also observed for gold and silver sols upon addition of gelatine. As example, a few series of experiments with Fe_2O_3-albumin sols are reproduced in Table 158 and graphically in Fig. 120. In this figure the abscissæ are concentrations of electrolyte, the ordinates the degree of flocculation in an arbitrary measure. The maximum attained corresponds to complete flocculation.

How great the sensitization may be appears from Table 159. It is particularly marked in the case of univalent anions, but is still noticeable with multivalent and organic ones.

To explain sensitization, as also coagulation, by hydrophilic sols we may start from the fact that the micellæ of hydrophobic sols take up those of the hydrophilic. An association similar to adsorption could be directly proved in the case of the interaction between the Fe_2O_3 micellæ and those

[1] Zeitschr. f. physik. Chemie, **89**, 306 (1915).

of the albumin solution. That the flakes separated from the Fe_2O_3-albumin sol contain albumin can even be recognized externally by their lighter colours.

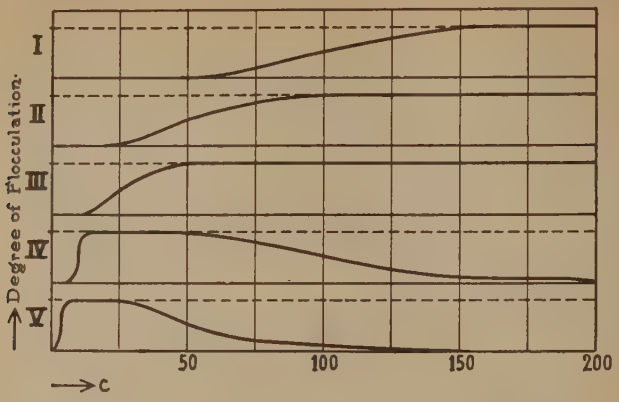


Fig. 120.—Sensitization of Fe_2O_3 Sol by Serum Albumin.

Table 158

Sensitization of the Coagulation of Fe_2O_3-Albumin Sols of different Content

Albumin solution dialysed 7 days; content 7·58 g. per litre. 50 c.c. of it became completely clear again on addition of 4 c.c. of Fe_2O_3 sol (content 17 g. Fe_2O_3 per litre). Pure Fe_2O_3 sol for comparison: 50 c.c. H_2O + 25 c.c. Fe_2O_3 sol.

NuCl Concentration (millimol per litre) (after dilution with the Sol).	I Pure Fe_2O_3 Sol.	II 50 c.c. Albumin Solution + 25 c.c. Fe_2O_3 Sol.	III 50 c.c. Albumin Solution + 15 c.c. Fe_2O_3 Sol.	IV 50 c.c. Albumin Solution + 7 c.c. Fe_2O_3 Sol.	V 50 c.c Albumin Solution + 4 c.c. Fe_2O_3 Sol.
1·56	—	—	—	—	Not coagulated, clear
3·13	—	—	—	Not coagulated, clear	Turbid
6·25	—	—	Not coagulated, clear	,,	Completely coagulated
12·5	—	Not coagulated, clear	,,	Completely coagulated	,,
25	—	,,	Turbid	,,	,,
50	Not coagulated, clear	Turbid	Completely coagulated	,,	Turbid, flakes
100	Turbid	Completely coagulated	,,	Turbid	Scarcely turbid
200	Completely coagulated	,,	,,	Scarcely turbid	Not coagulated, clear
1000	,,	,,	,,	—	—

TABLE 159

Sensitization of the Coagulation of Fe_2O_3-Albumin Sols by various Electrolytes

Electrolyte.	F.V. of Fe_2O_3 Sol [1] (millimol per litre).	F.V. of Fe_2O_3-Albumin Sol [1] (millimol per litre).
NaCl	37	1·2
$\frac{BaCl_2}{2}$ [2]	—	1·2
Na salicylate . . .	2·3	0·29
Na urate	0·75	0·18
K_2SO_4	0·59	0·29

It is found that the albumin distributes itself between the Fe_2O_3 particles and intermicellar liquid, the amount taken up increasing, with small concentrations, in proportion to the albumin content of the liquid and reaching a saturation at high concentrations. Similar adsorption isothermals are also known for the adsorption of the micellæ of other hydrophilic sols by other adsorbents (cf. p. 219). It is not a matter of a clean adsorption, for the albumin cannot be smoothly washed out by diluting the Fe_2O_3-albumin sol. Probably it becomes insoluble at the interface, and hence denatured, as has been observed in similar cases (cf. p. 537).

Coagulation by hydrophilic sols, as also sensitization, probably simply depends upon the fact that we are dealing with hydrophilic sols containing colloid ions,[3] and these ions discharge oppositely charged micellæ of hydrophobic sols just as do other oppositely charged ions. If the discharge goes far enough, coagulation takes place; if not, we have a sensitization, in which case an addition of electrolyte is still necessary to complete the flocculation. In favour of this view we have the fact that coagulation and sensitization have only been found in the case of hydrophilic sols,[4] which under the experimental conditions in question were able to yield oppositely charged colloidal ions, with a negative (feebly acid) gold sol, for example, gelatine, albumin, and casein, but not gum arabic; with a silver sol, gelatin and casein, but not soap and saponin. A feebly alkaline gold sol (prepared by the formaldehyde method) is neither coagulated nor sensitized by gelatine, since at this OH' ion concentration insufficient colloidal kations are present. But a sol of this kind is coagulated by a solution of clupeine sulphate,[5] the salt of a protamine, a protein which forms kations preferentially, even in alkaline solution. Since albumin and similar substances are amphoteric, they can doubtless provide in neutral solution sufficient colloidal kations and anions to sensitize or coagulate both positive and negative hydrophobic sols. Hence it may be entirely in

[1] These values are not strictly comparable. Two albumin solutions with 6·72 and 7·58 g. per litre resp. were used: to 50 c.c. of the first were added 4·5 c.c. Fe_2O_3 sol, to 50 c.c. of the second 4 c.c. Fe_2O_3 sol. Accordingly, the pure Fe_2O_3 sols contained 50 c.c. H_2O + 4·5 c.c. Fe_2O_3 sol and 50 c.c. H_2O + 4 c.c. Fe_2O_3 sol resp. The undiluted Fe_2O_3 sol was the same as Table 158.

[2] According to Table 113, p. 421, $BaCl_2$ has a F.V. only little different from NaCl.

[3] *Freundlich* and *Löning*, Kaiser Wilhelm Gesellschafts-Festschrift 1921, p. 82; further Gann, *loc cit.* p. 424.

[4] *Freundlich* and *Löning*, *loc. cit.* under [3].

[5] *Freundlich* and *Löning*, *loc. cit.* under [3].

agreement with this theory, that according to L. Michaelis and Rona [1] negative suspensions of mastic and kaolin, and according to Brossa and Freundlich [2] negative Mo_2O_5 sols behave towards albumin solutions in exactly the same way as the positive Fe_2O_3 sol. In contradiction it might be added that according to Henri [3] and his co-workers Fe_2O_3 sols are also sensitized by starch-solutions; but a starch solution is very poor in colloid ions (see p. 637). It may be, however, that the starch sol employed was not very pure, but contained amylopectin, a hydrophilic colloid which very distinctly forms colloid anions.

How the hydrophobic and hydrophilic primary particles are arranged in the mixed micellæ cannot yet be said with certainty. Probably the hydrophilic micellæ are on the exterior, although their size and amount are insufficient to completely enclose the hydrophobic core. It may be regarded as impossible that, conversely, the "excess" Fe_2O_3 particles enclose the albumin, for one can sensitize a Fe_2O_3-albumin sol prepared by adding a Fe_2O_3 sol to an albumin solution still more strongly by subsequently adding more albumin sol. This makes it probable that the albumin added later is related to the Fe_2O_3 in a manner similar to that added originally.

The distribution of the albumin between Fe_2O_3 micellæ and intermicellar liquid makes it intelligible why, with the same amount of albumin, the sensitization decreases with increasing amount of Fe_2O_3 (cf. Table 158, p. 584, and Fig. 120). A larger amount of Fe_2O_3 means a larger amount of adsorbent. From a solution of a given amount of albumin more albumin will on the whole be adsorbed by a larger amount of Fe_2O_3, but since the albumin concentration remaining behind in the liquid in equilibrium is smaller, the amount per gram of Fe_2O_3 must also be smaller. Hence the sensitization is necessarily smaller.

The sensitization by hydrophilic sols is a very general phenomenon. The action just mentioned, observed by Henri and his co-workers,[4] of starch solution on Fe_2O_3 sols is probably the first case of the kind. Then Neisser and Friedemann [5] found that a small amount of a gelatine sol renders a mastic emulsion sensitive to flocculation by NaCl. That glycogen acts in the same way as starch was observed by Mme. Gatin-Gružewska.[6] The strong sensitization of Fe_2O_3 sols by albumin sol was first qualitatively described by Pauli and Flecker.[7] Walpole [8] mentions that oil emulsions are coagulated by smaller concentrations of acid, if minute amounts of gelatin have been added. Also the influence earlier mentioned (p. 484) of small amounts of matter from the finger-tip in the coagulation of gold sols arises at least in part from a sensitization or coagulation by hydrophilic sols.

It follows from Table 158 and Fig. 120 that the difference between Fe_2O_3-albumin sols and pure aqueous Fe_2O_3 sols is not confined to sensitization. With Fe_2O_3-albumin sols, we observe, at higher electrolyte concentrations, renewed peptization instead of flocculation; that is, an irregular series

[1] Biochem. Zeitschr. **2**, 219 (1907); **5**, 365 (1907).
[2] *loc. cit.* p. 583.
[3] *V. Henri, Lalou, A. Mayer,* and *Stodel,* Compt. rend. d. l. soc. d. biolog. **55**, 1671 (1903).
[4] *loc. cit.* under [3].
[5] Münch. Med. Wochenschr. **51**, Nr. 11 (1903).
[6] Compt. rend. d. l. soc. d. biolog. **58**, 698 (1906).
[7] Biochem. Zeitschr. **41**, 470 (1912).
[8] Proc. Physiol. Soc. 1913, meeting of December 8.

appears, while this is not the case with pure aqueous sols. It arises from a peptizing action similar to that described (p. 579) for globulin. This is shown in the fact that, as in the latter case, the upper non-flocculating zone appears at a lower concentration, the more strongly adsorbable is the anion, and the higher its valency :

For	Cl'	ion about	100	millimolar.
,,	SO_4''	,, ,,	25	,,
,,	picrate	,, ,,	13	,,
,,	citrate	,, ,,	1·3	,,

In this upper non-flocculating zone the micellæ are, as we should expect, negatively charged ; we are therefore dealing with a peptization due to electric charge. One might be surprised that with pure Fe_2O_3 sols, so strongly dispersive an ion as the citrate ion (see p. 474) does not charge up and peptize even at high concentrations, while it does so readily in the presence of albumin. This may perhaps be partly caused by the pure Fe_2O_3 flocculi coarsening too rapidly when once coagulated, while the particles and envelopes of albumin which effectively separate the Fe_2O_3 particles prevent coarsening and crystallization, and greatly favour dispersion by a powerful peptizing agent. The strongly peptizing citrate ion seems to possess a general power of peptizing flakes consisting of hydrophobic and hydrophilic micellæ ; this was observed for flakes of Fe_2O_3 and glycogen, Fe_2O_3 and saponin, As_2S_3 and albumin, V_2O_5 and albumin, and others.[1]

Sensitization by hydrophilic sols is a very wide-spread phenomenon, which can also be applied in many ways. If one and the same Fe_2O_3 sol is sensitized by various hydrophilic sols under comparable conditions, previous experience shows that hydrophilic sols differ considerably in their sensitizing power. Very different concentrations of NaCl are necessary for flocculation. One may thus characterize a hydrophilic sol, following Windisch and Bermann,[2] by its *iron number*. They used this, for example, to distinguish the various colloid mixtures obtained by fractional ultrafiltration from beer, and difficult to distinguish by ordinary analytical means. It was found that a certain fraction, held back by an ultrafilter of a certain fineness of pore, is responsible for the foaming power of beer. The iron number of this fraction was then compared with those of various colloids preparable from malt or wort, and it was thus made probable that this property of beer must mainly be ascribed to the wort gum.

Reitstötter[3] found that albumins from various sera sensitize more strongly than the so-called paraglobulins[4] ; and the paraglobulins from antitoxic sera more strongly than those from normal or anti-bacterial sera, as Table 160 shows. For medical purposes, therefore, the determination of the iron number should be important.

The method worked out by Michaelis and Rona[5] for removing proteins

[1] *Brossa* and *Freundlich, loc. cit.*, p. 583.
[2] Wochenschr. f. Brauerei, **37**, 130 *et seq.* (1920).
[3] Zeitschr. f. Immunitätsforsch. **30**, 507 (1920).
[4] Paraglobulins are proteins which are salted out as globulins in semi-saturated $(NH_4)_2SO_4$ solution, but dissolve in electrolyte-free water [*Reitstötter*, Zeitschr. f. Immunitätsforsch. **30**, 468 (1920)].
[5] Biochem. Zeitschr. **2**, 219 (1907) ; **3**, 109 (1907) ; **4**, 11 (1907) ; **5**, 365 (1907) ; **7**, 329 (1908) ; **8**, 356 (1908) ; **14**, 476 (1908) ; *Rona* and *Oppler, ibid.* **13**, 121 (1908).

TABLE 160

Sensitization of a Fe_2O_3 Sol by various Proteins

Protein Hydrosol.	F.V. (millimol per litre).			
	NaCl.	$\frac{BaCl_2}{2}$	Na Salicylate	K_2SO_4.
Protein-free Fe_2O_3 sol	37·5	37·5	2·3	2·3
Albumin from human blood-serum . . .	0·29	0·29	0·097	0·097
Ox albumin	0·235	0·235	0·097	0·097
Horse albumin	0·235	0·235	0·097	0·097
Diphtheria albumin	0·235	0·235	0·097	0·097
Paraglobulin from human blood-serum . .	4·69	4·69	1·17	1·17
Ox paraglobulin	4·69	4·69	1·17	1·17
Horse paraglobulin	4·69	4·69	1·17	1·17
Dysentery serum paraglobulin (Shiga-Kruse)	2·34	2·35	0·586	0·29
Diphtheria ,, ,, ...	2·34	2·35	0·586	0·29
Tetanus ,, ,, ...	1·17	2·35	0·097	0·097
Fowl-cholera serum ,, ...	9·37	4·69	2·345	1·17
Swine-fever serum ,, ...	4·69	4·69	1·17	1·17

from liquids depends upon sensitization by hydrophilic sols. They added a Fe_2O_3 sol or a mastic emulsion or kaolin suspension to the natural protein solution containing electrolyte; the electrolytes present cause flakes consisting of micellæ of the hydrophobic sol and protein to separate, so that with a suitable excess of the hydrophobic sol the protein is completely removed. Although this flocculation is to be referred to a sensitization, the conditions of experiment are nevertheless distinctly different from those in the sensitization experiments hitherto described. Hitherto the serial order in which the interacting liquids were mixed was

Albumin solution + Fe_2O_3 sol + electrolyte solution . . (1)

In the protein precipitation experiments of L. Michaelis and Rona, on the other hand, it is

Albumin solution + electrolyte solution + Fe_2O_3 . . (2)

Two differences appear. First, flocculation occurs more quickly in the second than in the first case. In the first case, in the absence of electrolytes, the Fe_2O_3 micellæ can form with the albumin the amicronic micellæ of which the comparatively stable Fe_2O_3-albumin sol consists. In the second case, on the other hand, the Fe_2O_3 is immediately introduced into an electrolyte solution and flocculated without the amicronic micellæ with the albumin having been formed. For the same reason no upper non-flocculating zone is observed in Case 2, while in Case 1 it is so distinct (see Table 161).

The Fe_2O_3 behaves in case 2 as in pure aqueous solution, since it comes too quickly into contact with the electrolyte solution, which flocculates it completely before its micellæ have had time to unite with the albumin to amicronic particles. The amount of albumin taken up in Case 2 (protein precipitation) by the Fe_2O_3 particles curiously enough does not

TABLE 161

Influence of the Order of Mixing on the Coagulation of Fe_2O_3-Albumin Sols

5 c.c. albumin solution (7·58 g. per litre); 0·4 c.c. Fe_2O_3 sol; 1 c.c. NaCl solution

NaCl Concentration (millimol per litre) (after dilution by the sol).	Albumin Solution + Fe_2O_3 Sol + NaCl Solution.	Albumin Solution + NaCl Solution + Fe_2O_3 sol.
3·13	Turbid	Not coagulated, clear
6·25	Completely coagulated	Completely coagulated
12·5	,, ,,	,, ,,
25	,, ,,	,, ,,
50	Turbid, flakes	,, ,,
100	Scarcely turbid	,, ,,
200	Not coagulated, clear	,, ,,
500	—	,, ,,

differ very greatly from that taken up in Case 1, although in Case 2 obviously the opportunity for the formation of amicronic flocculi is not given.[1]

In the interaction between albumin solutions (and other hydrophilic sols) and heavy metal salts sensitization is also apparently not to be neglected. In any case this is supported by the fact that, according to Pauli's [2] experiments, albumin solutions as free as possible from salts are not flocculated by solutions of Zn, Cu, Hg, and Pb salts, while this is decidedly the case with those containing salts. Whether this depends rather upon the hydroxides contained in a state of colloidal division in the heavy metal salt solutions, than upon the interaction between albumin and heavy metal salt with the formation of chemical or adsorption compounds, is not yet settled. In any case, irregular series are also observed as in the case of the sensitization of Fe_2O_3 sols by albumin[3]; along with the coagulating action of the electrolytes a peptizing one is also found.

The Protective Action of Hydrophilic on Hydrophobic Sols

The flocculation and sensitization of a hydrophobic by a hydrophilic sol presupposes according to present experience two things. The micellæ of the hydrophobic sol must in a certain sense be present in excess, and the hydrophilic sol must contain colloid ions with charges opposite to those of the particles of the hydrophobic sol. If conversely the micellæ of the hydrophilic sol are present in excess, another effect is observed, which at first attracts more attention, and which one is more inclined to expect, namely a *protective* action of the micellæ of the hydrophilic upon those of the hydrophobic sol; that is to say, the sensitiveness of the hydrophobic sol towards electrolytes is more or less considerably decreased by the presence

[1] Among this group of phenomena must also be included the increased rate of fall of blood corpuscles in the blood in certain conditions, e.g. pregnancy, and which results from a partial discharge by oppositely charged colloids contained in the blood [see *Fåhraeus*, Biochem. Zeitschr. **89**, 355 (1918); *Linzenmeier*, Pflüg. Archiv, **181**, 169 (1920); **186**, 272 (1921)]. The same is true for the sensitization of suspensions of bacteria by the blood plasma of pregnant women [*Löwenthal* and *Berthau*, Zentralbl. f. Bakteriol. u. Paresitenkunde, I Abt. **83**, 315 (1919); *Vorschütz*, Pflüg. Archiv, **186**, 290 (1921).

[2] Beitr. z. chem. Physiol. u. Pathol. **7**, 541 (1906).

[3] See e.g. *Galeotti*, Zeitschr. f. physiol. Chemie, **40**, 492 (1903–04); *Pauli*, Beitr. z. chem. Physiol. u. Pathol. **6**, 233 (1905).

of the hydrophilic sol. Since metal sols under ordinary conditions of experiment contain a comparatively small number of micellæ, it is intelligible that the protective action of hydrophilic sols has been described first and foremost for these, but according to present experience it may appear with all hydrophobic sols. After Lottermoser and E. v. Meyer [1] had pointed out that protein protects silver sols from flocculation by electrolytes, Zsigmondy [2] in particular investigated the protective action of various hydrophilic sols upon red gold sols. He performed the experiments by allowing various small amounts of the hydrophilic sol (0·1 to 1 c.c.) to mix rapidly with 10 c.c. of a red gold sol (0·05 to 0·06 g. per litre) and then added 1 c.c. of a NaCl solution (10 per cent., i.e. about 2 N); the amount (in milligrams) of the disperse phase of the hydrophilic sol, which when contained in 10 c.c. of the solution just prevented the red colour of the gold sol from changing to blue (see p. 416) was determined. Zsigmondy's experimental conditions—rapid addition of the gold solution to the hydrophilic sol, addition of the NaCl three minutes after mixing—must be exactly reproduced, if generally comparable values are to be obtained. This amount Zsigmondy named the *gold number* of the hydrophilic sol, a value very suitable for distinguishing hydrophilic sols or for following changes in their properties (see p. 593).

The strength of the protection follows from the fact that about 0·01 mg. of active colloids such as gelatine protects 0·6 mg. of gold against NaCl containing 200 millimol per litre. Without gelatine a concentration of about 20 millimolar suffices to cause the red colour of the gold sol to change to blue in five minutes. Here, too, one can see that it is not easy to decide from the relative amounts of the micellæ of the two sols which is in excess. That different colloids differ greatly in their gold number is shown by Table 162. In it are also the "*rubin numbers*" determined by Wo. Ostwald,[3] that is, the amounts of colloid in grams per 100 c.c. solution

TABLE 162

Gold and Rubin Numbers of various Hydrophilic Sols

Sol.	Gold Number (in mg. per 10 c.c. Solution).	Rubin Number (in g. per 100 c.c. Solution).
Gelatine and other kinds of glue	0·005–0·01	0·025
Isinglass	0·01–0·02	—
Sodium caseinate	0·01	0·004
Hæmoglobin	0·03–0·07	0·008
Albumin	0·1–0·2	0·020
Gum arabic	0·15–0·25	—
Sodium oleate	0·4–1	—
Dextrin	6–20	—
Potato starch	about 25	about 0·2
Colloidal SiO_2	∞	—
Old colloidal SnO_2	∞	—
Mucus of quince seeds	∞	—

[1] Journ. f. prakt. Chemie, **56**, 242 (1897); see also *Lottermoser*, Zeitschr. f. physik. Chemie, **62**, 284 (1908).

[2] Zeitschr. f. analyt. Chemie, **40**, 697 (1901); *Zsigmondy* and *Fr. N. Schulz*, Beitr. z. chem. Physiol. u. Pathol. **3**, 137 (1902).

[3] Kolloidchem. Beihefte **10**, 234 *et seq.* (1919); see also Lüers, Kolloidzeitschr. **27**, 123 (1920).

which prevent the change of colour of a Congorubin sol in a manner similar to that of the gold sol; the concentrations were determined at which a distinct difference in colour could just be observed as compared with a Congorubin sol free from protective colloid. KCl served as electrolyte in a concentration of 160 millimolar. Similar colloid numbers may be determined with any other hydrophobic sol; Congorubin was chosen because an organic substance differs so much from gold in its material nature.

The supposition readily suggests itself, that the protective action is simply due to the adsorption of the micellæ of the hydrophilic sol on those of the hydrophobic, thus surrounding the latter, and transforming them as it were into micellæ of a hydrophilic sol, which is much less sensitive to electrolytes. That the protective colloid is taken up by the micellæ of the hydrophobic sol may be regarded as certain. Zsigmondy[1] demonstrated that a gelatine skin is formed upon gold foil, and it is also possible, using suitable gelatine sols, to observe ultramicroscopically that gelatine particles associate with gold particles. As opposed to coagulation and sensitization by hydrophilic sols, their protective action depends little or not at all upon their charge. As appears from Table 162, protective power is shown both by colloids such as gelatine and proteins, which also coagulate and sensitize, as also by such as saponin, which mostly do not. With the latter the protective action increases regularly with increasing concentration, from the smallest concentration of the hydrophilic sol, as has been shown for the interaction of a saponin sol with a Carey Lea silver sol.[2] With colloids, such as gelatine, which coagulate and sensitize in small concentrations, it was also shown with the same silver sol that coagulation only takes place at small concentrations. If the concentration is increased, the coagulative action gives place to the protective action fairly suddenly. It may even be recognized externally by the fact that no colour change is observed in the sol, whereas in the coagulation range the greenish-brown sol changes to black. The kataphoretic migration velocity of the originally negative Ag particles alters as follows. In the range of coagulation the charge decreases with increase in gelatine content, without the particles being reversed in charge. As soon as we reach the range of protective action, the negative charge of the particles again increases, without reaching a value as high as that which the micellæ had in the pure sol.

It follows from this that the protective action certainly does not depend upon a particularly strong charge being communicated to the particles. Further it is accordingly probable that the particles of the hydrophobic sol are enveloped in a certain sense by micellæ of the hydrophilic, for thereby the behaviour of the charge is easiest to explain. As long as the colloid kations of the gelatine are present in a certain excess as compared with the negative silver particles, their positive charge causes a discharge of these particles; but as soon as the concentration has become so great that they can completely envelop them, the possibility exists that the colloid ions may lie with their positive ends upon the negative Ag particles, while the other ends of these amphoteric colloid particles, which as anions are capable of carrying negative charges, project into the liquid. Hence the negative charge of the protected sols and the fairly sudden appearance of the protective action.

Although a certain adsorption is a presupposition for the protective action, the adsorbability of the hydrophilic micellæ still does not appear

[1] Kolloidchemie, 3 Aufl., p. 360.
[2] *Freundlich* and *Löning*, *loc. cit.* p. 585.

to be the sole condition, but it should also depend on their spatial arrangement at the interface, on the properties of the skins formed there, and in the case of proteins, for example, of chemical changes due to denaturing, and so on. This makes it intelligible that the protective action is not readily reversible. Thus Zsigmondy [1] found that $\frac{15}{1,000}$ mg. of gelatine dissolved in 23 c.c. of water did not act protectively on 10 c.c. of a gold sol; but it did so, when the same amount dissolved in 3 c.c. of water was added first, and the remaining 20 c.c. of water afterwards. That it does not depend alone upon the adsorbability must also be concluded from the fact that gelatine protects so much more strongly than, say, soap; one must assume, in view of the strong capillary activity of soap, that it is more freely adsorbed than gelatine, and the disproportionality becomes still more striking when we recollect that the molar concentration of the soap is greater than that of the gelatine. The strength and toughness of the protective envelopes, the way in which they are anchored to the hydrophobic particles, all these circumstances exert an influence. Perhaps a connexion also exists between the rigidity of a sol (cf. p. 539) and its protective action. Anyhow, in order to elucidate the relations, the influence of the nature of the coagulator will also have to be tested. Thus Heinz [2] found the following:—While alkaline stannic acid sols only feebly protect gold sols against NaCl, they protect more strongly against HCl; with NaCl the protective action increases the greater the amount of alkali present in the tin sol; with HCl, on the contrary, it decreases greatly with increase in alkali content. One would expect to meet a clear connexion between protective action and adsorbability first in the case of substances which do not differ too greatly. In fact, Biltz [3] found with a number of dextrins a clear parallelism between their adsorbability by Fe_2O_3 and their protective action upon a gold sol. Thus the order of adsorbability was amylodextrin > achroodextrin > some commercial dextrins, and the gold numbers, the reciprocal value of which is a measure of the protective action, had the opposite order.

If it is a matter of adsorption, it is to be expected that, with increasing content of the protective colloid, the protection will reach a limit, if only for the reason that the adsorption tends towards a saturation. Whether at high concentrations of protective colloid the stability of the protected hydrophobic sols is as great as that of the pure hydrophilic colloid acting as protector, requires investigation. It is not in contradiction with the view of an adsorption that a certain time must pass before the protective action reaches its full effect. For, since the diffusion of the micellæ of a hydrophilic sol is slow, a perceptible time elapses before the adsorption equilibrium has been set up (cf. the slow setting up of adsorption equilibrium at the surface towards the gas-space, p. 533).

It is also in agreement with the view of an adsorption that, leaving gelatine out of account, the order of the protective colloids in the case of gold is so similar to that in the case of Congorubin. Here the chemical difference between the two sols is the greatest imaginable. Further with this agrees the fact that the three colloids gelatine, gum arabic, and dextrin exert upon a gold sol a protective action in the same order as that in which

[1] Kolloidchemie, 3rd Ed., 1920, p. 361.

[2] *Heinz*, "Ueber Kolloide Zinnsäuren wechselnden Alkaligehalts." Dissertation, Göttingen, 1914, p. 28 *et seq.*

[3] Zeitschr. f. physik. Chemie, **83**, 683 (1913).

they inhibit the catalysis of H_2O_2 by a Pt sol[1]; that inhibitions of this kind are undoubtedly to be referred to adsorption, has been explained earlier (p. 495).

All the influences exerted by electrolytes upon hydrophilic sols must also be noticeable with protected sols, in particular also the above described (p. 579) peptizing action at high electrolyte concentrations. In dealing with strongly adsorbable and multivalent ions, one should always take into consideration the fact that at high concentrations they peptize instead of coagulate, even in those cases where the hydrophobic sol alone is not peptizable. This action is more probable than the other, namely, that they might peptize the hydrophilic colloid away from the interface, and make the hydrophobic micellæ again easily coagulable. At quite large electrolyte concentrations, again, salting-out may occur.

The Importance of the Action of Protective Colloids

There is hardly a property of colloids which is so frequently and generally met with, and which is so frequently employed, as the protective action of hydrophilic sols.[2] In the first place hydrophilic sols may be distinguished and characterized, and changes in their properties may be followed, by means of their protective action. Up to the present the gold number (with NaCl as coagulator) has almost exclusively been used for this purpose. It is not impossible that in some instances another hydrophobic sol, or another coagulator, may be more suitable for measuring protective action. Schulz and Zsigmondy[3] applied the gold number successfully in their first investigations in order to characterize the various protein fractions of white of egg. Globulins protected most strongly. In the case of albumin three fractions were distinguished: one crystallized comparatively easily, and protected feebly; a second was amorphous and strongly protecting; and a third was also amorphous, and in small concentrations did not protect, but coagulated. If the view put forward above (p. 585) is correct, the latter would be a protein which forms sufficient kations even in faintly alkaline gold sols to produce coagulation, and perhaps approaches the more strongly basic protamines in properties. With the serum proteins investigated by Heubner and Jacobs,[4] this differentiation was less successful, since all fractions were readily accompanied by a substance which, instead of protecting, coagulated.

That the gold number characterizes the hydrophilic colloids in a direction different from that of the iron number, is important. That this is so follows from the foregoing considerations (p. 591)—in connexion with which it should be remarked that the iron number depends upon the charge on the colloid ions, whilst the gold number does not, or only to a small extent—and also from an investigation by Reitstötter.[5] He investigated the behaviour of various natural and toxic sera. It appeared that this depended essentially upon their content of different proteins. Albumins protect

[1] *Gróh*, Zeitschr. f. physik. Chemie, **88**, 414 (1914); *Iredale*, Journ. Chem. Soc. **119**, 109 (1921).

[2] Likewise, hardly another is so old. For the so-called drinkable gold of the old apothecaries is none other than a protected gold sol, prepared by reduction of gold chloride with oil of rosemary [*Vanino* and *Hartl*, Ber. d. deutsch. chem. Ges. **39**, 1696 (1906); *Vanino*, Journ. f. prakt. Chemie, **73**, 575 (1906)].

[3] *loc. cit.* p. 590.

[4] Biochem. Zeitschr. **58**, 352 (1913).

[5] Zeitschr. f. Immunitätsforsch. **30**, 468 (1920).

least, and euglobulins [1] most, strongly; paraglobulins are intermediate. Sera, such as tetanus serum, swine-fever serum, dysentery serum, and others, which contain no albumin, but only globulins, accordingly protect particularly strongly, more strongly than the gelatines, which are otherwise the strongest protectors (cf. Table 162); normal horse serum and diphtheria serum, which, with a small globulin content, also contain albumins, protect much less strongly. The anti-bodies, which alter the iron number in a characteristic manner (cf. p. 587), did not change the gold number when the globulin content remained the same.

C. Lange [2] has pointed out that in cases of syphilis the cerebro-spinal fluid coagulates gold sols, while this is not the case with the fluid from a healthy individual. According to Reitstötter, all these experiments have not stood the test of stricter experimental criticism. It appears to him, however, quite possible that globulins are contained in the fluid in cases of illness and, mixed with them, the substances which coagulate gold sols instead of protecting them, and which made their presence so strongly felt in the above-mentioned experiments of Heubner.

As an example [3] in which the change with time of a sol showed itself in the gold number, it may be mentioned that, after standing for one day, the gold number of a gelatine solution becomes sensibly greater (the protective power therefore smaller) than that of the fresh solution; and this change is relatively greater with a dilute solution.

Further, the most generally useful method of preparing colloidal solutions depends upon protective action. One can, indeed, assert, that for every substance difficultly soluble in a dispersion medium a protective colloid may be found which enables its dispersion to be effected. Paal [4] systematically investigated the preparation of colloidal solutions of this kind over a large field, and prepared a series of important sols. He used as protective colloids particularly *protalbic acid* and *lysalbic acid* and their alkali salts. These are protein derivatives prepared by hydrolysis.[5] Albumin is heated with a solution of alkali, and the protalbic acid precipitated in flakes by acidification with acetic acid. In order to obtain lysalbic acid, the solution is acidified with sulphuric instead of acetic acid, filtered from the precipitated protalbic acid, neutralized and evaporated; it is then again acidified with sulphuric acid, and the foreign electrolytes removed by dialysis. The aqueous solutions of these acids and their salts are, like the soaps, dextrins, etc., semi-colloidal. Thus, lysalbic acid, which is soluble in water, dialyses perceptibly through parchment paper and gives in about 1·8 per cent. solution a depression of the freezing-point of 0·05, which corresponds to a molecular weight of about 700 to 800. On the other hand the solutions are turbid, in higher concentrations viscous and syrupy, dry up to horn-like masses and undoubtedly contain colloidal ions and doubtless also micellæ of the free acid or other products of hydrolysis, quite similarly to soap solutions (cf. p. 566).

[1] Euglobulins are the true globulins which, as opposed to paraglobulin, cannot be peptized in pure water, but only in electrolyte solutions.

[2] Zeitschr. f. Chemotherapie, Bd. 1, Nr. 1; Berl. Klin. Wochenschr. 1912, Nr. 16.

[3] *Menz*, Zeitschr. f. physik. Chemie, **66**, 133 (1909).

[4] Ber. d. deutsch. chem. Ges. **35**, 2206 (colloidal Ag_2O); 2219 (HgO); 2224 (Ag); 2236 (Au) (1902); *Paal* and *Amberger*, *ibid.* **37**, 124 (1904); **38**, 1398 (1905) (Pt metals); *Paal* and *Voss*, *ibid.* **37**, 3862 (1904) (silver salts); *Paal* and *C. Koch*, *ibid.* **38**, 526 (Se); 534 (Te) (1905); *Paal* and *Leuze*, *ibid.* **39**, 1545 (CuO), 1550 (Cu) (1906).

[5] *Paal*, Ber. d. deutsch. chem. Ges., **35**, 2195 (1902).

With the aid of these substances Paal prepared, in particular, sols of the metals, metallic hydroxides and oxides, of many salts, of selenium and tellurium, etc. The colloidal solutions thus obtained may be regarded as examples of sols the stability of which depends upon the presence of protective colloids. They are insensitive to electrolytes and to heat, may be thawed unchanged after freezing, dry up to lamellæ which easily redissolve in weak alkali, and retain this property for a long time. It is surprising what small amounts of organic material suffice to make large amounts of metal colloidally soluble. Paal prepared with sodium lysalbate a silver sol, which he flocculated with acetic acid ; the latter also flocculates pure solutions of lysalbic acid, doubtless a salting-out effect. The separated flakes dried in a desiccator to heavy, metallic grains with a greenish shimmer, containing 93 per cent. of silver, and peptizable in dilute NaOH solution. Only after two years had they lost this property to a large extent.[1] By fresh addition of sodium lysalbate complete peptizability could be restored in another case, after the flakes had become too impoverished in protective colloid by repeated flocculation.[2]

The method of preparing these sols may be described, in general, as follows. If we add to the solution of the salt of the heavy metal, the sol of which is to be obtained, a solution of protalbic or lysalbic acid or the sodium salt of one of them, the heavy metal salts of the acids separate in the form of caseous flakes ; these dissolve in NaOH or KOH. If the alkali be removed by dialysis, a dark-coloured sol remains behind, which is to be regarded as the sol of the metallic oxide or hydroxide. By reduction with hydrazine hydrate—sometimes it is sufficient to warm the sol, since the acids in question act as reducing agents—the metallic sols are obtained.

Of sols prepared with the aid of protalbic or lysalbic acids or of other proteins or protein derivatives, the following may be mentioned. The colloidal solutions extensively employed in medicine, such as those of silver (collargol, protargol, and others), of bismuth (bismon), of sulphur (sulfoid), and many others,[3] are all sols containing protective colloids, mostly derivatives of proteins. Paal and Leuze [4] succeeded in obtaining, by reduction of CuO sols containing lysalbic or protalbic acids, red copper sols the colour of which passed into blue on concentration or coagulation. They were therefore to a large extent similar in their behaviour to gold sols ; this may be referred to a similarity in absorptive and reflective power of the metals. The sol of palladium hydride [5] is important. It may be obtained by heating a dried palladium sol with protalbic acid as protective colloid in a current of hydrogen at 100–140°. Externally it does not differ from a palladium sol, but is distinguished from this by being an effective reducing agent, which is extensively employed in organic preparation. In order to effect reduction by means of colloidal palladium hydride, it is not necessary to start from the finished sol ; the desired effect is also attained by treating the substance to be reduced with hydrogen in the presence of a palladium sol.[6] Some of the reactions which may be effected with palladium sols

[1] Ber. d. deutsch. chem. Ges. **35**, 2234 (1902).
[2] Ber. d. deutsch. chem. Ges. **35**, 2235 (1902).
[3] See a compilation by *R. O. Herzog*, Die Eiweisskörper, in *Ullmann*, Enzyklop. d. techn. Chemie, IV, 522 et seq. (1916).
[4] *loc. cit.* p. 594.
[5] *Paal* and *Amberger*, Ber. d. deutsch. chem. Ges. **38**, 1398 (1905).
[6] *Paal* and *Amberger*, Ber. d. deutsch. chem. Ges. **38**, 1406, 2414 (1905).

will be dealt with later (p. 598). Sols of dyes have also been obtained in this way, e.g. indigo sol with the aid of sodium lysalbate.[1]

The advantage offered by lysalbic and protalbic acid does not apparently depend so much upon their unusually great protective action in the sense of a particularly small gold number. According to Gortner [2] their gold number is about equal to that of gum arabic, and about ten times smaller than that of gelatine. The fact that, as acids, they may be conveniently brought into interaction with metals, and the advantages which the semi-colloids have in general for peptization (cf. p. 604) will also be particularly decisive for their applicability.

Among the sols investigated by Paal are also those with micellæ, the chief constituent of which usually crystallizes so rapidly, that it can only with difficulty be obtained in a disperse form. In the case of the action of chloroacetic ester upon sodium malonic ester in benzene, Michael observed [3] that a yellowish red turbid liquid appeared from which crystalline NaCl could be precipitated by the addition of water. Paal [4] showed that this was probably due to the formation of a sodium chloride sol in benzene, the ethenyl tricarboxylic ester which is formed, or one of its derivatives, acting as protective colloid. In a similar manner he prepared a colloidal solution of sodium bromide in benzene.

In sufficiently concentrated solutions of *gelatine* (about 5 per cent. in the warm) and other hydrophilic sols, such as *gum*, etc., it is possible to prevent the separation of practically every precipitate which is difficultly soluble in water, and to retain it colloidally dispersed in solution. Thus sols of many difficultly soluble substances, such as halides, sulphates, and chromates, may be obtained.[5] This effect is not, without further consideration, to be regarded as identical with that exerted by hydrophilic sols on already existing hydrophobic sols. On the contrary, we have here not only a protective effect of the kind above described, but the colloids also influence the velocity of formation of nuclei and the velocity of crystallization of the separating solid, as considered above (p. 503) in discussing the preparation of gold sols. Too little is known concerning the change in the velocity of formation of nuclei to be able to take it into account with certainty at the present time. Much more is known concerning the change in the velocity of crystallization, which Marc investigated closely in aqueous solution (cf. p. 337). Crystallization is completely stopped when considerable supersaturation still exists in the solution, large crystals cannot be formed, the separated solid is therefore very finely crystalline or solid-amorphous, and hence easily remains in solution colloidally. Hence we may here once more, partly by way of repetition, go into the points already shortly discussed (p. 338).

In the preparation of silver bromide gelatine emulsions for photographic plates, the influence of the colloid on the size of grain and other properties of silver bromide has been made use of to the greatest possible extent in

[1] *Möhlau* and *Zimmermann*, Zeitschr. f. Farben- und Textilchemie, **2**, 25 (1903).
[2] Journ. Amer. Chem. Soc. **42**, 595 (1920).
[3] Ber. d. deutsch. chem. Ges. **38**, 3217 (1905).
[4] Ber. d. deutsch. chem. Ges. **39**, 1436, 2859 (1906); further *Paal* and *Zahn*, *ibid.* **42**, 277 (1909).
[5] *Lobry de Bruyn*, Rec. d. trav. chim. d. Pays-Bas, **19**, 236 (1900); Ber. d. deutsch. chem. Ges. **35**, 3079 (1902); see also e.g. *Feilmann* [$BaSO_4$ sols with aid of casein; Chem. News, **98**, 310 (1909)].

order to give it the required properties as regards sensitivity to light and so on.[1]

Facts are known concerning silver halogen compounds which put beyond doubt the taking-up of hydrophilic colloids such as albumin, gelatine, gum, dyes, and others. Reinders (cf. p. 339) was able to prove this directly in the case of the silver halide crystals which separate from ammoniacal silver solution. Further, he was able to show that even at great dilutions of the hydrophilic solution gelatine, albumin, etc., were taken up by the crystals; the latter are then considerably more sensitive to light than those separated from pure solution. Thus in the case of gelatine a concentration of 0·1 mg. per litre could still be detected in the increased sensitivity to light of the AgCl which separated. The strong retarding action exerted by gelatine upon the reaction of solid AgCl with dissolved reducing agents [2] depends upon its retarding the rate of crystallization of the separated silver. In preparing gold sols, colloidally dissolved substances such as soaps, oils, colloidal sulphur, and others, are able to actually stop the further growth of gold nuclei which have been added.[3]

The impurities which in preparative chemistry so frequently prevent the separation of crystals of a desired substance are likewise generally "tarry" substances, hydrophilic colloids which, in small concentrations, prevent crystallization. They are removed by heating the solution with animal charcoal, which adsorbs the colloids.

If preparative chemistry has as its goal the preparation of crystals, Nature usually strives for its purposes after amorphous solid or very finely crystalline substances. She often attains this end through the presence of hydrophilic colloids which hinder the crystallization of substances which otherwise easily separate in a crystalline form. The following may be cited as an example: the white scales on the wings of a genus of butterflies, *Pieris*, consist very largely of pure uric acid, which is prevented from crystallizing by some substance, probably a colloid.[4] By treatment with animal charcoal the substance preventing crystallization may be removed. The stone-like concretions (gall-stones, kidney-stones, and the like), which are formed in the organism in cases of disease, likewise belong throughout to structures such as are formed upon separation of difficultly soluble substances from solutions of hydrophilic colloids. The structure of these stones, the finely crystalline or amorphous form of the difficultly soluble substances, may be largely referred to the influences which take effect in separation from such sols.[5] It is intelligible that in connexion with these structures the influence of colloids attracted the attention of physicians comparatively early. It thus happens that, apart from earlier observations, one of the earliest colloido-chemical monographs, that of Ord,[6] dealt with these phenomena. In it are found good observations concerning the influence of gum arabic and other colloids upon the forms of separation of calcium carbonate and other difficultly soluble salts. Ord did not arrive at an explanation of this phenomenon; this first became possible after Marc's investigations upon the adsorption of colloids and their influence upon the velocity of crystallization.

[1] *Lüppo-Cramer*, "Photographische Probleme," Halle, 1907.
[2] *Reinders* and *van Nieuwenburg*, Kolloidz. **10**, 36 (1912).
[3] *Hiege, loc. cit.* p. 503.
[4] *Hopkins*, Phil. Trans. **186**, B, 661 (1895).
[5] *Schade, loc. cit.* p. 341.
[6] "The Influence of Colloids on Crystalline Form and Cohesion," London, 1879.

It may be added that the soft, velvety nature of ice-cream [1] depends upon a small content of gelatine or similar colloids, which on account of their influence upon the velocity of crystallization only permit the growth of very small crystals.[2]

It is not only colloidally dissolved organic substances which are capable of this protective action. It is also known in the case of inorganic hydrophilic sols. To these phenomena depending on protective action belongs, again, one of the oldest products of colloid chemistry, the so-called *Purple of Cassius*, which Kunkel introduced for the production of ruby gold glass. It was obtained by reducing a gold chloride solution with stannous chloride. E. A. Schneider,[3] and particularly Zsigmondy,[4] showed that this depends upon the formation of micellæ which are composed of the gold particles resulting from the reduction and the stannic acid formed by oxidation. The following experiment of Zsigmondy's may be taken as a proof of this. If a gold sol prepared by reduction with formaldehyde be mixed with a freshly prepared colloidal stannic acid solution, a purple of Cassius is obtained which has quantitatively the same properties as a product of like composition produced by reduction as above described. The stannic acid is here the protective colloid. It protects gold from flocculation by electrolytes and makes it peptizable; just as the gel of stannic acid is easily peptized in water when moistened with ammonia, so also is purple of Cassius. But an aged stannic acid sol is not (as appears from Table 162, p. 590) able to act protectively.

Lottermoser [5] has also used stannic acid as protective colloid in the preparation of sols of other metals (copper, silver, mercury, and bismuth), and L. Wöhler [6] has pointed out that the red colour which appears upon the reduction of platinum solutions by stannous chloride depends upon the formation of colloidal platinum protected by stannic acid. He also points out the curious circumstance that silver also, like platinum and gold, gives an unstable red colour on reduction in solutions of stannous salts, which again is to be referred to colloidal silver (cf. the red colour of highly disperse Carey Lea sols, p. 508).

Silicic acid sols appear, in general, to have a smaller tendency to exert protective action.[7] Küspert,[8] however, describes a certain protective effect with water-glass solutions, and Graf Schwerin[9] states that electrolytically purified silicic acid sols, as free as possible from electrolytes, render metallic sols produced in them by reduction or electrical disintegration more stable; however, in the case of gold a blue sol is obtained.

Reactions and Catalytic Actions of Metal Sols prepared with Protective Colloids

As already mentioned, the use of protected metallic sols as catalysts is important in preparative organic chemistry; this is especially true concern-

[1] See Clayton, II B.A. Rep. on Coll. Chem., p. 116.
[2] *Alexander*, Kolloidzeitschr. **4**, 86 (1909).
[3] Zeitschr. f. anorg. Chemie, **5**, 80 (1894).
[4] Lieb. Ann. **301**, 361 (1898).
[5] "Ueber anorganische Kolloide." Stuttgart, 1901, p. 53 *et seq.*
[6] Kolloidzeitschr. **2**, Suppl. 1, III (1907); **7**, 243 (1910).
[7] *Zsigmondy*, Zeitschr. f. analyt. Chemie, **40**, 699 (1901).
[8] Ber. d. deutsch. Chem. Ges. **35**, 2815, 2816, 4066, 4070 (1902).
[9] D.R.P. Nr. 285,025 and 295,222.

ng reductions with palladium hydride sols. For this purpose it is not necessary, as previously mentioned, to start with the finished palladium hydride sol, but an effective reduction can be attained by allowing hydrogen to act upon the substance to be hydrogenated in the presence of palladium sols; it is sometimes sufficient to allow the hydrogen to bubble through, more frequently it is necessary to shake the reaction mixture with hydrogen. Thus nitrobenzene is reduced to aniline in alcoholic solution in the presence of a palladium sol at room temperature, when hydrogen is passed through it.[1] Among other substances that can be hydrogenated in this manner, we may mention fumaric acid,[2] ethylene,[3] and particularly the soaps[4] and esters[5] of unsaturated fatty acids; the fats are employed for this purpose in the form of an emulsion prepared with gum arabic.[6] Hydrogen may also be determined by gas volume measurements by shaking the mixture of gases with a solution containing, besides palladium, a rapidly reducible substance; picric acid has proved useful for this purpose.[7]

Palladium is not the only platinum metal which is able to activate hydrogen in this way; similar reducing actions may also be obtained with protected platinum and iridium sols, but, calculated on the weight of metal, their action is weaker. The activation with osmium and silver sols is much smaller, with gold and copper sols none was observed.[8]

Paal's sols can only be used for reduction in neutral or alkaline solution, since they are too unstable in acids. In order to remove this defect, Skita[9] uses palladium sols protected by gum arabic. With many reducible substances, such as aldehydes and ketones, it is not necessary to add the finished palladium sol. It may be allowed to form during the reduction; a solution of palladium chloride containing gum is mixed with the aqueous-alcoholic solution of the organic substance and hydrogen is then passed in. Other substances containing hydrogen are not suitable for the production of the sol. With these the finished palladium or platinum sol must be added at the start.[10]

Of other reactions of these sols, the following deserve mention. Acetylene is also freely adsorbed by palladium sols, and undergoes complicated transformations on the micellæ.[11] Platinum sols behave similarly, while no adsorption of this gas was observed upon iridium and osmium sols.[12] An oxidation reaction which has been investigated is that of CO to CO_2 by sols of palladium, platinum, iridium, and osmium.[13] Paal points out

[1] *Paal* and *Amberger*, Ber. d. deutsch. chem. Ges. **38**, 1406, 2414 (1905).
[2] *Paal* and *Gerum*, Ber. d. deutsch. chem. Ges. **41**, 2273 (1908).
[3] *Paal* and *W. Hartmann*, Ber. d. deutsch. chem. Ges. **42**, 2239 (1909).
[4] *Paal* and *K. Roth*, Ber. d. deutsch. chem. Ges. **41**, 2282 (1908).
[5] *Paal* and *K. Roth*, Ber. d. deutsch. chem. Ges. **42**, 1541 (1909).
[6] Concerning further reductions of inorganic substances as well, see *Paal* and *Gerum*, Ber. d. deutsch. chem. Ges. **42**, 1553 (1909); *Paal* and *Hartmann*, *ibid.* **42**, 3931 (1909); *Paal* and *Oehme*, *ibid.* **46**, 1297 (1913); *Paal*, *W. Hartmann* and *Brünjes*, *ibid.* **47**, 2202 (1914); *Paal* and *Büttner*, *ibid.* **48**, 220 (1915); *Paal* and *Hohenegger*, *ibid.* **48**, 275 (1915).
[7] *Paal* and *W. Hartmann*, Ber. d. deutsch. chem. Ges. **43**, 243 (1910).
[8] *Paal* and *Gerum*, Ber. d. deutsch. chem. Ges. **40**, 2209 (1907); *Paal* and *A. Schwarz*, *ibid.* **48**, 994, 1202 (1915); **51**, 640 (1918).
[9] Ber. d. deutsch. chem. Ges. **42**, 1627 (1919); *Skita* and *H. H. Franck*, *ibid.* **44**, 2862 (1911).
[10] *Skita* and *W. H. Meyer*, Ber. d. deutsch. chem. Ges. **45**, 3579 (1912); see also *ibid.* **45**, 3589 (1912).
[11] *Paal* and *Hohenegger*, Ber. d. deutsch. chem. Ges. **43**, 2684 (1910).
[12] *Paal* and *A. Schwarz*, Ber. d. deutsch. chem. Ges. **48**, 1195 (1915).
[13] *Paal*, Ber. d. deutsch. chem. Ges. **49**, 548 (1916).

that it is scarcely permissible to interpret this process generally, as Heinr. Wieland [1] does, as a hydration and subsequent removal of hydrogen. For palladium Wieland was able to show that CO_2 is formed from CO even in the absence of oxygen, and explains this upon the basis of a reaction

$$CO + H_2O = C\begin{matrix}H\\ \diagup\\ \diagdown\\ O\end{matrix}OH = CO_2 + H_2;$$

that is, a hydration to formic acid and a removal of hydrogen by palladium. There is nothing to prevent this explanation from being retained for the sols of palladium and platinum, since they are able to activate hydrogen; but for the sols of iridium and osmium, for which this is scarcely or not at all the case, one would rather prefer to consider a direct oxidation of the CO by oxygen.

The catalysis of oxy-hydrogen mixture by palladium and platinum sols has likewise been followed by Paal and his co-workers.[2] Since it has also been investigated by Ernst for an unprotected Bredig platinum sol (cf. p. 499) a comparison might teach us much concerning the influence of the protective action. Unfortunately the experiments are not sufficiently extensive to allow anything certain to be said regarding the cause of the observed differences. With the unprotected sol there is a maximum velocity when H_2 and O_2 are present in concentrations corresponding with the reaction, a diminution of the velocity when either gas is in excess; with protected sols, on the other hand, an acceleration of the reaction by the presence of excess of hydrogen, a retardation by excess of oxygen. It appears to be clear that the velocity of the reaction is smaller with protected sols. McBain [3] also states this in comparing the oxidation of chromous chloride, using in one case an unprotected sol, and in the other one protected with gelatine.

On the other hand, Rideal [4] emphasizes that the reaction velocity apparently shows a maximum for a certain content of protective colloid. He followed the velocity of reduction of the Na salt of phenyl propiolic acid by H_2 in presence of Pd and Pt sols, which were either unprotected or protected with increasing amounts of gum arabic. The maximum velocity of reduction was observed with a Pd sol when 1–2 mg. of protective colloid were associated with 10 mg. of metal, with a Pt sol with 4 mg. to 10 mg. Rideal would like to follow Bancroft [5] in explaining this maximum by the protective colloids also acting, as we shall discuss below (p. 601), as peptizing agents and so enlarging the interface available for catalysis. The maximum occurs through the superposition of this favourable influence upon one that inhibits the action. In view of the facts mentioned above an inhibitory effect is probable, if only because the protective colloid is doubtless adsorbed and tends to diminish the reduction velocity at the interface either by displacing the reacting substances or by retarding the diffusion.

Poisoning by foreign substances is also met with again in the case of protected metal sols; that due to mercury is very strongly marked in the case of the catalysis of oxy-hydrogen mixture and in reduction processes;

[1] *Ber. d. deutsch. chem. Ges.* **45,** 679 (1912).

[2] *Paal* and *W. Hartmann*, Journ. f. prakt. Chemie, **80,** 337 (1909); *Paal* and *A. Schwarz, ibid.* **93,** 106 (1916).

[3] "Die Zersetzung des Chromochlorürs mit Kolloidem Platin." Diss., Heidelberg, 1909, pp. 57–8.

[4] Journ. Amer. Chem. Soc. **42,** 749 (1920).

[5] Journ. Phys. Chem. **20,** 85 (1916).

both metallic mercury and mercuric oxide act in this way.[1] They always act in a state of colloidal dispersion, for, as will be discussed shortly (cf. p. 603), both mercury and mercuric oxide pass into colloidal solution when shaken with platinum and palladium sols, protected by salts of protalbic acid. Here the cause of the poisoning has fortunately been discovered; the mercury amalgamates with the Pt metal and thus decomposes or prevents the formation of its hydride. This may be shown directly by the fact that mercury liberates the hydrogen from a sol of palladium hydride.[2] Hence both in the case of the catalysis of oxy-hydrogen mixture and of the reduction processes the formation of the metallic hydride is manifestly a necessary preliminary to catalysis. The decomposition of H_2O_2 under the influence of the sols mentioned is not visibly influenced by mercury, a sign that in this case the adsorption of hydrogen is not decisive for the reaction.

The Peptizing Action of Hydrophilic Sols

Many hydrophilic sols not only protect a colloidal dispersion already existing, but are also active peptizing agents, by means of which substances in mass can be colloidally dispersed with a comparatively small expenditure of mechanical energy. This is especially known in connexion with the soaps. It can be particularly clearly observed when the soap is only formed by the reaction between the substances to be dispersed and the dispersion medium. Thus, Donnan[3] performed the following experiment. He used a pipette similar to the stalagmometer, the lower end of which was bent upwards and drawn out to a point. The pipette was filled with the liquid to be dispersed, an oil, and the point dipped into a vessel which contained the dispersion medium, water or a faintly alkaline aqueous solution. When the oil contained fatty acid, the amount between two marks on the pipette was emulsified into many drops in water containing alkali, but this did not happen when the oil was as free as possible from acid.

Table 163

Influence of Soap upon the Emulsification of Oil

Substance to be Dispersed.	Number of Drops in Pure Water.	Number of Drops in 0·001 N NaOH.
Purified neutral olive oil	55	58
Commercial acid olive oil	58	331

The soap formed at the interface by the interaction of fatty acid and alkali strongly depresses the interfacial tension (cf. p. 536) and causes the formation of small drops. These drops do not coalesce, since the layer of soap at the interface acts as protective colloid. Indeed, the adsorbed layer of soap favours every increase in the interface; it fixes it, as it were; for the interfacial tension is small, and when by mechanical means depressions and contractions of form are produced in the liquid to be dispersed, they do not, on account of the low tension, disappear again. Indeed, one may, with Donnan, assume an influence which actually opposes the coalescence

[1] *Paal* and *W. Hartmann*, Ber. d. deutsch. chem. Ges. **51**, 711 (1918); concerning the effect of other metallic oxides besides HgO see *Paal* and *Hartmann*, *ibid.* **51**, 894 (1918).
[2] *Paal* and *Steyer*, Ber. d. deutsch. chem. Ges. **51**, 1743 (1918).
[3] Zeitschr. f. physik. Chemie, **31**, 42 (1899).

of the drops, and even divides them up further. This is particularly permissible in the case of soap solutions and other semi-colloids, in which the micellæ are so small or so flexible, that we may assume the protective layer to be comparatively easily mobile. The interfacial tension of the liquid surface covered with soap solution is smaller than that of the interface free from soap solution or poorer in the latter. If two drops collide, the concentration of the adsorbed protective colloid between them, say the soap, is increased; the interfacial tension is still further lowered. The larger interfacial tension at other parts of the interface causes particles at the surface to stream from places of low to those of high tension. This means an increased repulsion of the drops, a deepening and increased contraction of depressions which may have been formed.

If, instead of the dilute alkali, a soap solution is allowed to act upon a pure liquid such as oil or the like, the state of affairs is quite similar. For now the adsorption of the soap causes a depression of the interfacial tension and all that follows therefrom. By hydrolysis small amounts of fatty acid are also formed in the soap solution, which are then dissolved by the oil. By shaking with toluene fatty acid may be removed from the soap solution.[1] As long as equilibrium exists between the soap and the fatty acid split off from it, this fact can change nothing in the final state caused by the action of the soap upon the interface oil—aqueous solution.

Upon this peptization depends the detergent power of soap solutions.[2] The impurities, particularly fats, but also solid particles, which stick to the article to be washed either on account of their fatty nature, or even otherwise, are peptized by the soap in the manner described and thus removed. Mechanical treatment—rubbing, beating and the like, serves to produce the fine division of the dirt, which is then fixed by the adsorbed layer of soap. The strong formation of foam is also favourable. The peptized particles pass in part to the surface liquid—air, and so cannot easily again come in contact with the object being washed.

The chemical theory of the detergent action of soaps, frequently suggested earlier, which assumed a hydrolysis of the fats by the alkali content of the soap, may be regarded as confuted. Against it, in the first place, there is, as proved by McBain's experiments, the small alkali concentration of soap solutions (cf. p. 565), which is quite insufficient for a rapid saponification. Then Spring[3] showed that when soot or iron oxide which has been carefully freed from grease by benzene, and which can be suspended in water, is filtered through paper, it is retained by the latter. By washing the filter with soap solution, both the soot and the iron oxide can be readily removed, since the particles are peptized. Here we have a detergent effect without any fatty matter coming into question. The importance of these experiments of Spring's is not lessened by the fact that, according to P. Ehrenberg and K. Schultze,[4] they must be interpreted differently. That the soot becomes wettable by treatment with benzene depends less upon fatty

[1] See particularly *Reychler*, Kolloidzeitschr. **12**, 277 (1913).

[2] See especially *Spring*, Bull. d. l. Soc. chim. d. Belg. **24**, 17 (1910); Kolloidzeitschr. **4**, 161 (1909); **6**, 11, 109, 164 (1910); *Reychler, loc. cit.*; and also *Hillyer*, Journ. Amer. Chem. Soc. **25**, 511 (1903). See also the summary by *F. Goldschmidt*, "Handbuch der Chemie und Technologie der Öle und Fette," Leipzig, 1911, Bd. III, p. 396, especially p. 433 *et seq.*

[A short bibliography is also given in II B.A. Rep. on Coll. Chem., p. 67.]

[3] *loc. cit.* under [2].

[4] Kolloidzeitschr. **15**, 183 (1914).

impurities being removed than upon the removal of adsorbed layers of air ; the soot can also be made wettable by pressing it together strongly, and thus removing the air-films. Further, Spring regards the adherence of the soot particles to the filter too exclusively as an adsorption by the filter fibres, and their removal by washing with the soap solution too exclusively as a displacement adsorption ; the adsorption of the soap by the soot is supposed to be so strong as to loosen the connexion between soot and paper. Hence, according to Spring, soot suspensions to which soap has been previously added readily pass through the filter. As Ehrenberg and Schultze show, a sieving action of the filter also comes in. It is possible to prepare highly disperse soot suspensions, which pass the filter even without soap, if only extremely fine soot particles are taken, for example, those which are found in the foam from soot suspensions. The adsorption of soap is naturally important, but it works not only directly by preventing the attachment of the soot particles to the paper, but also in so far as it peptizes the coarser particles of soot into their single micellæ ; the micellæ which have become finer now pass through the filter, while the coarser ones originally present were held back by the pores of the filter.

Not less striking is the confutation by the following experiment of Reychler.[1] He prepared cetylsulphonic acid $C_{16}H_{33}SO_3H$ and its alkali salts. Their aqueous solutions show a great similarity to soap solutions ; they froth copiously, show a high conductivity, separate on salting out in the form of jellies, and so on. In contradistinction to the soaps, cetylsulphonic acid itself is not so difficultly soluble as the higher fatty acids, but gives a soap-like colloidal solution. This solution—an acid soap solution, as it were—exercises a detergent effect like ordinary soap. Hence it does not depend upon a reaction due to alkali.

Of other powerfully protective colloids, which can also readily act as peptizing agents, the sodium salts of *protalbic* and *lysalbic acids* may be mentioned. With their aid mercuric oxide and the hydroxides of iron, zinc, and copper can easily be brought into colloidal solution. Similarly, these oxides and hydroxides may also be peptized by a protected metal sol, such as a palladium sol protected by sodium protalbate. Like these oxides, metallic mercury itself may also be brought into colloidal solution by shaking with a palladium sol of this kind, which does not succeed when the sols of the protalbates are used alone. In the latter case the metal amalgamates with the mercury.[2] In the same way we obtain a colloidal solution of gold amalgam when a Paal gold sol is shaken with mercury.[3]

The *humic acids* and their salts also belong to the group of peptizing colloids. They are technically important, for their presence renders possible the ceramic process of *clay casting*. This arises from the fact that clays and kaolins containing some humus substances [4] can be stirred up with a little alkali to readily flowing pastes and poured into plaster of paris moulds. According to Neubert,[5] who in particular has elucidated these

[1] Kolloidzeitschr. **12,** 278 *et seq.* (1913).

[2] *Paal* and *W. Hartmann,* Ber. d. deutsch. chem. Ges. **51,** 736, 894 (1918).

[3] *Paal* and *Steyer,* Kolloidzeitschr. **23,** 145 (1918) ; **25,** 21 (1919).

[4] On the detection of colloids in clay by means of their staining with fuchsin, see e.g. *Endell,* Kolloidzeitschr. **5,** 244 (1909).

[5] Kolloidchem. Beihefte, **4,** 261 (1913) ; see further *H. Hirsch,* Tonindustrie-Zt. 1904, p. 492 ; *M. Böttcher,* "Über die Verflüssigung des Tons durch Alkali." Diss., Dresden, 1908 ; *Spangenberg,* "Zur Erkenntnis des Tongiessens." Diss., Darmstadt, 1910. [See Searle, III B.A. Report on Colloid Chemistry, pp. 113 to 153, for a general account of clay from a colloido-chemical standpoint. (Trans.)]

phenomena, we must take the following processes into account. In the first place there is the suspending action of adsorbed OH′ ions upon negative particles, already frequently referred to (p. 474). It was possible to prove directly the adsorption of OH′ ions in small concentrations according to the ordinary isothermal, and further, that adsorption is favoured by the presence of humous substances; this was, moreover, also the case when alkali was adsorbed by charcoal + humous substances instead of by charcoal alone. The humous acids and the salts arising from them by the action of alkali likewise peptize as do soaps. They are particularly necessary since, initially distributed as dry gels through the mass of the clay, they form the preliminary condition for the extensive disintegration of the coarser particles into finer ones. Without their presence the state of division does not become fine enough. At higher concentrations of alkali a stiffening of the fluid clay at first takes place. For this two circumstances are responsible. In the first place, that at high alkali concentrations the negative particles of clay are flocculated (see p. 422); but then water is abstracted from the liquid, since considerable quantities of humous substances lying in the interior of the clay particles undergo imbibition. This action upon deeper-lying layers also causes the curious reliquefying which follows upon the stiffening. The alkali humate abundantly supplied from the interior can again peptize the clay particles, and by the interaction with these deep-lying humous particles the alkali concentration also decreases and leaves the range in which it exerts a sensible coagulating effect. At still larger concentrations of alkali the paste remains stiff. Sufficient humous substances can no longer be supplied at these concentrations, the humic acid salts remain unadsorbed, and pass into solution, and enough alkali no longer disappears to allow the concentration to be removed from the flocculating range.

There are various reasons why, apparently, only a comparatively limited number of hydrophilic sols exert this peptizing effect. In the first place, it presupposes that the interfacial tension is lowered sufficiently strongly; the molar concentration must be high enough for this, and hence the molecular weight must not be too great. The latter is also necessary for the reason that with too slow a diffusion of the particles the adsorption and the movements at the interface described above (p. 601) do not take place rapidly enough.

Perhaps we ought to take into account for the peptizing and protective powers of the hydrophilic sols a completely different property, namely their rigidity (cf. p. 539). The certain inner rigidity of these sols must act more decidedly than ordinary viscosity in preventing the association of the particles and in separating particles adhering together by introducing between them as it were elastic fluid layers. This idea is suggested particularly by the decided peptizing and protective action of the gelatines, the capillary activity of which is by no means very decidedly marked. Thus also H. N. Holmes and Child [1] emphasize the fact that when petroleum is emulsified by gelatine in water no adsorption of the gelatine can be detected,[2] and that with the same amount of gelatine very different amounts of petroleum may be peptized. It has not yet been investigated

[1] Journ. Amer. Chem. Soc. **42**, 2049 (1920).

[2] Upon emulsifying benzene in water by aid of soap, *Briggs* [Journ. Phys. Chem. **19**, 210 (1915)] on the other hand was able to prove an adsorption of the soap at the interface.

whether a relation exists between the rigidity of a sol and its peptizing and protective power, and whether both properties alter in the same sense with change in the $H^{\cdot}$ ion concentration.

When it is a matter of one liquid being emulsified in another with the aid of a peptizing agent, the question arises, upon what does it depend that one liquid becomes the dispersion medium, and the other disperse phase ? Experiments and discussions by Wa. Ostwald,[1] Brailsford Robertson,[2] Fanto and Stritar,[3] Bancroft,[4] Newman,[5] and Freundlich and Gann,[6] lead to the following picture of the phenomena. The liquid which is present in great excess necessarily becomes the dispersion medium or continuous phase. But there exists a fairly extensive range of proportions within which either liquid may, in principle, become the continuous phase. The critical proportions at which the continuous phase becomes disperse because the drops of the disperse phase unite and become continuous, can obviously only be reached when these drops touch one another as closely as possible. If we assume equally large drops, this happens with a ratio of disperse to continuous phase of 74·04 to 25·96.[7] Between 26 and 74 per cent., therefore, both emulsions are, in principle, possible.

Which liquid preferentially becomes dispersion medium depends particularly upon the nature and quantity of the peptizing agent. This must form a uniform coating around the drops of the disperse phase. It is then probable that this envelope will turn its convex, i.e. larger, interface towards that liquid in which it can undergo imbibition or with which it can react chemically[8]; an envelope in which hydrophilic properties predominate will therefore tend to turn its convex surface to the water as continuous phase; a more hydrophobic one towards the non-aqueous liquid as continuous phase (cf. Fig. 121). As a matter of fact, hydrophilic colloids, such as gelatine, gum, and others favour the formation of emulsions in water; hydrophobic, such as the resin soaps,[9] soot,[10] and others, that of water emulsions in oil.

Yet a further detail comes into play when the peptizing agent is not present in over-large amount.[11] It is then more favourable that it should be present chiefly in the phase which is to form the dispersion medium. The drops of the disperse phase, the total volume of which is assumed to be small, can then build up their protective envelopes by adsorption from a comparatively large store of peptizing agent. If, on the contrary, the peptizing agent is contained in the liquid which is to become the disperse

[1] Kolloidzeitschr. **6**, 103 (1910); **7**, 64 (1910).
[2] Kolloidzeitschr. **7**, 7 (1910).
[3] Journ. f. prakt. Chemie, **81**, 564 (1910).
[4] Journ. Phys. Chem. **17**, 501 (1913); **19**, 275 (1915). He takes particular account of experiments by *Holde* [Kolloidzeitschr. **3**, 270 (1908)].
[5] Journ. Phys. Chem. **18**, 34 (1914).
[6] Internat. Zeitschr. f. phys.-chem. Biologie, **2**, 1 (1915); see further also *Groschuff*, Kolloidzeitschr. **9**, 257 (1911); *Briggs*, Journ. Phys. Chem. **19**, 210 (1915); *Briggs* and *H. Schmidt*, *ibid.* **19**, 478 (1915); *Briggs*, *ibid.* **24**, 121 (1920); *Briggs*, *Du Cassé* and *L. H. Clark*, *ibid.* **24**, 147 (1920); *M. H. Fischer* and Frl. *Hooker*, Kolloidzeitschr. **18**, 129, 242 (1916).
[7] *Wa. Ostwald*, *loc. cit.*; see also *Beijerinck*, Kolloidzeitschr. **7**, 17 (1910).
[8] *Bancroft*, *loc. cit.* under [4]; Newman, *loc. cit.* under [5].
[9] *Holde*, *loc. cit.* under [4].
[10] *Schlaepfer*, Journ. Chem. Soc. **113**, 522 (1918); *W. C. Moore*, Journ. Amer. Chem. Soc. **41**, 940 (1919).
[11] *Freundlich* and *Gann*, *loc. cit.* under [6].

phase, each drop has available only the small amount which was present in it from the beginning. For this reason substances present in water, such as gelatine, gum, and so on, will favour the formation of aqueous emulsions, while those dissolved in the non-aqueous liquid, such as resin soaps and the like, will make this liquid the continuous phase. It thus arises that, in opposition to what is generally observed, solutions of spermaceti and other substances in chloroform, when shaken with dilute aqueous alkali, give emulsions and colloidal solutions of the aqueous phase in chloroform as dispersion medium.[1]

The previous history and the peculiarities of the experimental arrangement are likewise important for the formation of one or other emulsion. Thus Wa. Ostwald found that when the emulsion was produced by energetic stirring of the two liquids in a cylindrical vessel, the liquid which wetted the walls of the vessel from the outset, preferentially became the continuous phase; evidently because the drops of the liquid which coated the wall coalesced upon striking it, while the drops of the non-wetting liquid rebounded unaltered and formed the disperse phase.

For the stability of such emulsions it is important, as Pickering[2] in

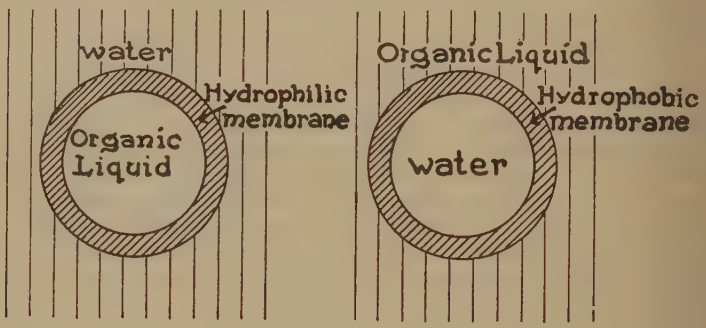


Fig. 121.

particular has emphasized, that the peptizing agent should form tough, indeed actually solid, films around the drops, and so directly hinder their coalescence. For this it is not necessary that the films should be continuous. It suffices when they consist of many solid particles. The soaps are particularly effective for the reason that they have a decided tendency to give solid precipitates of this kind, which are flexible in threads (cf. p. 614), and thus give the films a certain elasticity. The same circumstances are of importance for the stability of foams and will be considered in part under that heading in more detail (cf. p. 791).

When a solid surface is wetted by an emulsion, it is always the continuous phase which determines the wetting. An emulsion with water as the continuous phase wets like water, one with oil as continuous phase like oil. This fact is of importance in many technical questions, such, for instance, as the impregnation of wood with tar oils.[3]

During the transition of an emulsion of oil in water to one of water in oil in which the critical ratio is passed, curious changes in the viscosity

[1] *Freundlich* and *Gann, loc. cit.* p. 605.
[2] Kolloidzeitschr. **7**, 11 (1910).
[3] *Wa. Ostwald, loc. cit.* p. 605.

appear according to Brailsford Robertson.[1] Just in the critical region the viscosity of oil in water increases rapidly. The drops of oil are forced so close together, that only exceedingly fine, indeed ultramicroscopic films of the continuous phase separate them from one another. The displacement of the liquid particles in these fine lamellæ requires, according to Poiseuille's equation, a considerable amount of work and causes a high viscosity (cf. also Hatschek, p. 542). But as soon as the oil drops have coalesced and the emulsion of water in oil has been formed, we have water drops separated by considerable spaces filled with oil, and the viscosity assumes values, as the amount of the water phase decreases, which differ little from that of pure oil.

The Transformation of Hydrophilic into Hydrophobic Sols

If a hydrophobic sol is so altered by the addition of a protective colloid that it becomes insensitive to electrolytes, that it is easily repeptized after drying, that it is fairly viscous, and froths, this really means nothing else than that a hydrophobic sol has been transformed into a hydrophilic sol. The converse transformation of a hydrophilic into a hydrophobic sol is also important and occurs frequently. It would, however, appear that no general cause can be given to which this transformation may be attributed, but that very different influences operate from case to case.

Substances are known which can transform a hydrophilic sol or a hydrophilic suspension or emulsion into a hydrophobic sol exactly as the protective colloids in a certain sense change hydrophobic into hydrophilic sols. Unfortunately these phenomena have been almost exclusively observed upon structures of an entirely biochemical character, in the case of which explanation is not easy. In the first place we have the transformation of the decidedly hydrophilic suspensions which can be prepared in the case of many bacteria, into the hydrophobic suspensions of the corresponding *agglutinin-bacteria*.

The flocculation of these suspensions was investigated particularly by Neisser and U. Friedemann,[2] and then by Bechhold,[3] and by Buxton and his co-workers.[4] The suspension is prepared by suspending the culture of the bacteria in water containing formaldehyde: this kills the bacteria. It is purified by repeatedly centrifuging and resuspending it, or by dialysis. In order to obtain agglutinin-bacteria, the bacteria are first treated with agglutinin serum, that is, with the serum of an animal which has been poisoned with these bacteria. In order to obtain it in suspension one proceeds just as with the bacteria.

How decided is the transformation of the bacteria suspensions behaving as hydrophilic colloids into the hydrophobic suspension of the agglutinin-bacteria may be seen from Table 164. It is taken from experiments by Bechhold on typhus bacteria, the figures representing the flocculation values in millimols per litre necessary to flocculate the bacteria suspensions in 24 hours at 37°.

In the case of an emulsion of bacteria, alkali and alkaline earth salts produce no flocculation, but the salts of the earth and heavy metals and

[1] *loc. cit.* p. 605.
[2] München mediz. Wochenschr. **51**, Nr. 11 (1903); **51**, Nr. 19 (1904).
[3] *loc. cit.* p. 429.
[4] *Buxton* and *Schaffer*, Zeitschr. f. physik. Chemie, **57**, 44 (1907); *Buxton* and *Teague*, *ibid.* **57**, 64 and 76 (1907).

TABLE 164

Comparison of the Coagulation of Typhus Agglutinin-bacteria with that of ordinary Typhus Bacteria

Electrolyte.	F.V. of the Bacteria (millimol per litre).	F.V. of the Agglutinin-bacteria (millimol per litre).
NaCl	∞	25
$NaNO_3$	—	25
$\frac{Na_2SO_4}{2}$	—	55
KOH	∞	∞
HCl	0·5	1
HCOOH	1	1
$AgNO_3$	25	1
$MgSO_4$	∞	1·3
$CaCl_2$	∞	2·3
$BaCl_2$	∞	2·5
$Ni(NO_3)_2$	—	1·3
$HgCl_2$	1·3	0·25
$\frac{Al_2(SO_4)_3}{2}$	0·08	0·08
$\frac{Fe_2(SO_4)_3}{2}$	0·2	0·04

the acids do so very strongly; this is a behaviour such as may occur with a hydrophilic sol (cf. p. 618). On the other hand, the agglutinin-bacteria present a picture largely corresponding to that of the hydrophobic sols (cf. Table 112, p. 420); prominence of adsorbability and valency, approximately equally strong action of equivalent amounts, no flocculation by alkalis, sensibly greater flocculation by $H^{\cdot}$ ions and by the ions of heavy metals.

Also in the flocculation experiments of Buxton and Teague [1] with solutions of dyes the more hydrophobic character of the agglutinin-bacteria suspensions appears in the fact that they are flocculated by sensibly smaller concentrations than the bacteria suspensions.

With the agglutinin-bacteria, irregular series are further observed (cf. p. 429), not only with aluminium and iron salts, but also with acids. This has not yet been found with other negative hydrophobic sols, but the counterpart, namely the irregular series with OH' ions, has been observed in the case of a positive sol such as Fe_2O_3 (cf. p. 430). With the strong adsorption and charging action of $H^{\cdot}$ ions this behaviour is quite to be expected.

How the agglutinin really acts is not known with certainty. Its taking-up by the bacteria entirely follows the rules of adsorption. But the adsorption is decidedly specific, in a manner which has not yet been realized in the case of non-biological adsorption (cf. p. 538). Whether the taking up of the agglutinin suffices in itself to confer hydrophobic properties on the surface of the bacteria, or whether a chemical action, which first produces this change, follows the "adsorption," is an open question. One might think of regarding the action of agglutinin as a

[1] Zeitschr. f. physik. Chemie, **60**, 489 (1907).

sensitization (cf. p. 583). The specific behaviour might then depend upon a special spatial geometrical form of the surface of the bacteria and of the agglutinin particles.[1] In the case of a sensitization it is to be expected that the kataphoretic migration velocity of the agglutinin bacteria would be smaller than that of the original bacteria.

That the micellæ of a hydrophilic sol may become hydrophobic by a chemical transformation is well exemplified by protein sols. If a dilute, faintly acid, but otherwise as far as possible electrolyte-free solution of egg-albumin is heated, it becomes cloudy and opalescent, because the albumin particles are denatured. This denaturing is, as we shall see immediately, a chemical process, in which the albumin doubtless suffers an internal rearrangement. The *sol of the denatured albumin particles* is now, in contradistinction to the original albumin, decidedly hydrophobic, so that it is already flocculated by the salts of the alkali and alkaline-earth metals. Hardy [2] first observed this ; more detailed experiments are due particularly to Miss Chick and C. J. Martin.[3]

It is true that the sol of the denatured albumin still shows properties which remind one of those of the original hydrophilic sol, and which serve to distinguish it from real hydrophobic sols. Thus the amphoteric nature of albumin clearly appears in the fact that by simple alteration of the $H^{\cdot}$ ion concentration an iso-electric point of the denatured albumin micellæ may be determined, both by means of kataphoretic experiments and also by the optimum of flocculation (cf. p. 574). It is found to be about $3{\cdot}8 \times 10^{-6}$ for denatured serum albumin, while natural serum albumin has a value of about 2×10^{-5}. The denatured albumin is thus less acid than the original. With ordinary hydrophobic sols, such as those of the metals, sulphides, and so on, it is well known that it is impossible to produce a reversal of charge by means of $H^{\cdot}$ ions and to determine an iso-electric point by the method of Michaelis.

With sols of denatured albumin the fact appears, however, that, as in the case of ordinary hydrophobic sols, the flocculation of the particles is not conditioned by the $H^{\cdot}$ ion alone, but also by the other anions and kations present ; thus active kations—those of high valency such as $Al^{\cdot\cdot\cdot}$ ions, and those of the heavy metals, such as $Cu^{\cdot\cdot}$, $Ni^{\cdot\cdot}$—displace the optimum of flocculation towards the basic side, that is in the region of lower $H^{\cdot}$ ion concentration, active anions such as SO_4'', CNS' and others towards the acid side, that is in region of higher $H^{\cdot}$ ion concentration.[4] The whole behaviour is thus again entirely similar to that described earlier (p. 266) in connexion with electrosmotic experiments of Bethe and Toropoff on protein membranes.

It has not yet been tested how far this displacement of the optimum of flocculation runs, in general, parallel to the displacement of the isoelectric point of the denatured protein, as can be determined by means of kataphoresis (cf. p. 570) ; and then, whether the iso-electric point of the natural, not denatured hydrophilic sols of proteins and other substances is a definite function of the $H^{\cdot}$ ion, and whether it does not also depend, like that of the sol of denatured protein, upon the nature of other ions present. If

[1] *Diesselhorst* and *Freundlich*, Internat. Zeitschr. f. phys.-chem. Biologie, **3**, 54–55 (1916).
[2] Zeitschr. f. physik. Chemie, **33**, 385 (1900).
[3] Journ. of Physiol. **45**, 261 (1912) ; Kolloidchem. Beihefte **5**, 101 *et seq.* (1913).
[4] *Michaelis* and *Rona*, Biochem. Zeitschr. **94**, 225 (1919).

a similar influence should appear as in the case of sols of denatured protein, the argument and formula of L. Michaelis reproduced on p. 571 would not be strictly correct, since it assumes sole dependence upon the concentration of the $H^{\cdot}$ ion.

On both sides of the iso-electric point, with small OH' ion as with small $H^{\cdot}$ ion concentrations, the denatured protein particles are peptized, and, as in the case of hydrophobic sols, to a negative sol by OH' ions, and to a positive one by $H^{\cdot}$ ions.[1] With the negative sol the flocculation by electrolytes depends particularly upon the adsorbability and valency of the kations, with the positive one on the corresponding properties of the anions. That the coagulating ions, especially the particularly active ones, reverse the charge of the particles again in higher concentrations again corresponds to the behaviour of hydrophobic sols; strongly adsorbable and multivalent kations render the originally negative sol containing OH' ions positive again; strongly adsorbable and multivalent anions render the originally positive sol containing $H^{\cdot}$ ions negative again with redispersion of the particles. This reversal of charge and repeptization appear to go particularly easily with such protein sols. Even univalent inorganic ions, such as those of chlorine, effect it readily. This depends greatly upon the chemical nature of the particles. Thus, Miss Chick and C. J. Martin[2] found that denatured particles of serum albumin may be recharged and dispersed even by small concentrations of various ions, for example Cl' ions, while this is less easily done with denatured egg-albumin, and in any case multivalent anions are necessary. Examples of the strongly peptizing effect of anions on the micellæ of sols consisting of, or containing, protein, have already been referred to (p. 587); particularly also in the case of Fe_2O_3-albumin sols. These results entirely correspond to the results of Michaelis and Rona just referred to (p. 609): active kations coagulate strongly in faintly alkaline solution; in this active anions peptize, while they only coagulate in acid solution.

Of important processes occurring in nature the curdling of milk and the clotting of blood depend, in principle, upon nothing else than the transformation of a hydrophilic emulsion or a hydrophilic sol, as the case may be, into a hydrophobic one.

It is difficult in the case of *milk* to form, on the basis of available investigations, a clear and detailed picture of the processes to be taken into account. As peptizing agents hydrophilic colloids (proteins such as casein and others) come into consideration, and further also salts such as citrates. The hydrophilic envelopes are doubtless transformed into more hydrophobic ones by chemical influences, which have the character of ferment reactions, as, for example, by the action of rennet; and multivalent kations, such as the $Ca^{\cdot\cdot}$ ion present in milk, then produce coagulation. The binding of the Ca by the casein and a possible displacement of the $H^{\cdot}$ ion concentration are probably not to be neglected in connexion with these processes. The degree of dispersity of the fat drops in milk and their influence upon its properties have been accurately investigated by Wiegner.[3]

In the case of the clotting of blood the whole mechanism is so difficult to disentangle, the number of substances concerned apparently so great,

[1] *Hardy, loc. cit.* p. 609; Miss *Chick* and *C. J. Martin, loc. cit.* p. 609.

[2] Journ. of Physiol. **45,** 276 *et seq.* (1912); Kolloidchem. Beihefte **5,** 117 *et seq.* (1913).

[3] Kolloidzeitschr. **15,** 205 (1915).

that we are not yet able to analyse the process by colloidal chemistry into its elements.[1]

Chemical Reactions of the Micellæ of Hydrophilic Sols

It has already been repeatedly pointed out that the micellæ of many hydrophilic sols are very reactive. In the case of the proteins, gelatines, etc., one can assume that every foreign substance added is able to enter into reaction, and, in particular, that reactions with the dispersion medium, water, occur. This renders very difficult the investigation of many of these sols, for example, enzyme solutions, since they change in one's hands. Up to the present only a few reactions of such micellæ have been investigated in detail. They are also so numerous and varied that they call for a separate treatment which lies outside the scope of this book. It is, however, perhaps useful even to consider more closely a well-defined reaction of this sort which has been more fully investigated, since its peculiarities have perhaps general importance.

The reaction in question is the long-known denaturing of proteins upon heating in aqueous solution, to which we have already frequently referred. The processes which occur were originally regarded as a single phenomenon which was referred to as the heat coagulation of the proteins which took place at the coagulation temperature characteristic for each protein. But Hardy [2] and Pauli and Handovsky [3] had already pointed out that we are dealing with two independent processes, the denaturing of the protein, a reaction which probably takes place between the protein and the water, and the flocculation of the denatured protein, which depends in the manner just described upon the presence of $H^{\cdot}$ and other ions. Miss Chick and C. J. Martin [4] separated the two processes from one another and examined them separately. That it depends upon an interaction with water follows from the fact that, according to the experiments of these investigators, dry crystalline egg-albumin is completely soluble in water, and hence not denatured, after heating for 5 hours at 120°.

Accordingly they followed the denaturing of aqueous protein sols. At a suitable small concentration of ammonium sulphate the flocculation of the denatured protein takes place so quickly that by following the change in protein content, which is estimated in samples filtered off, the velocity of denaturing alone is followed. Both with hæmoglobin and egg-albumin the reaction was found to be of the first order, provided that, in the latter case, the $H^{\cdot}$ ion concentration, which otherwise alters in course of the reaction, was kept constant by the presence of a weak acid (boric acid) in the solid form.

This denaturing reaction, and not merely the subsequent flocculation, is greatly dependent upon the $H^{\cdot}$ and OH' ion concentration and upon the neutral salt content. An increase in either $H^{\cdot}$ or OH' ion concentration increases the velocity of denaturing. Miss Chick and C. J. Martin explain this on the grounds that the resulting protein ions have a greater affinity for water than has the neutral protein. Conversely, neutral salts inhibit denaturing. This partly depends upon the fact that, through the neutral

[1] *P. Morawitz* in *Oppenheimer*, "Handbuch d. Biochemie," II, 2, p. 40 *et seq.*
[2] Journ. of Physiol. **24**, 158, 288 (1899).
[3] Beitr. z. chem. Physiol. und Pathol. **11**, 425 (1908).
[4] Journ. of Physiol. **40**, 404 (1910); **43**, 1 (1911); **45**, 61, 261 (1912); Kolloidchem. Beihefte **5**, 49 (1913).

salts, the H· and OH′ ion concentrations of the protein are displaced, being decreased in both cases. The main part of the inhibition is to be ascribed to a pure action of the salt, which is doubtless connected with the fact that salts bind water and thus withhold it from reaction with the protein. Here also a more exact knowledge of the lyotropic phenomena, that is, of hydration equilibria, will be required for further elucidation.

The extraordinarily great influence of temperature is remarkable. It is true that Arrhenius's formula

$$\log k = -\frac{A}{T} + B$$

may also be applied here, where k is the reaction velocity constant and A and B are constants; but both have values which deviate widely from those ordinarily observed. With hæmoglobin A = 29,400, B = 83·7; with egg-albumin A = 76,350 and B = 218·6. In ordinary chemical reactions A usually has values of 6000 to 10,000 and B of about 30. This means that in the case of hæmoglobin the velocity of denaturing increases 16-fold between 60° and 70°, with egg-albumin 564-fold between 69° and 79°, while the velocity is, of course, usually doubled for a rise of temperature of 10°.

A particularly strong temperature effect is specially common in the case of reactions of micellæ and of substances of high-molecular weight. The velocity of the destruction of emulsin increased 7·14-fold for a rise of 10° (between 60° and 70°) (Tammann [1]); for the action of trypsin Bayliss [2] found for a rise of temperature of 10° a 5·14-fold increase. Still larger temperature coefficients were observed by Famulener and Madsen [3] and Madsen and Streng [4] for the velocity with which hæmolysins and agglutinins are destroyed on warming with water.

Perhaps this behaviour is connected with the fact that, according to v. Halban,[5] true unimolecular reactions, i.e. reactions in which molecules of different kinds do not collide, but molecules of one kind become unstable in themselves, have larger temperature coefficients than ordinary reactions (a value of A in Arrhenius's formula of 10,000 to 30,000). One might then suppose that in the reactions above referred to, the micellæ do not react with the molecules of water outside, but with those present in large amount within the micellæ themselves. Since the latter water molecules are already bound in a manner quite different from those outside, it is comprehensible that the temperature coefficient has a value so completely different. According to this we are dealing in the case of these reactions, in which the main constituents of the micella and water are always concerned, to a very large extent with intramolecular reactions. What these reactions are is still an open question, perhaps the formation of an intramolecular salt in which the amount of bound water changes.

The large temperature coefficient leads to the consequence, already often referred to (see p. 527), that a threshold value exists. Below a certain temperature (dependent on the H· ion concentration and electrolyte content) denaturing proceeds very slowly, and at one only slightly higher so rapidly that one may speak of a definite coagulation temperature and use it to characterize the various proteins. It is, however, only conditionally

[1] Zeitschr. f. physik. Chemie, **18**, 426 (1895).
[2] "Nature of Enzyme Action" (Longman's Biochemical Monographs), 1908.
[3] Biochem. Zeitschr. **11**, 186 (1908).
[4] Zeitschr. f. physik. Chemie, **70**, 263 (1909).
[5] Zeitschr. f. physik. Chemie, **67**, 129 (1909).

applicable on account of the dependence upon the composition of the solution.[1]

From the dependence of denaturing upon temperature we may conclude that this process takes place at room temperature, although exceedingly slowly. In actual fact ageing protein sols always deposit some protein which has become insoluble, and hence may be regarded as denatured.[2]

Apparently various external conditions can also greatly accelerate this reaction, but it must still remain an open question whether it is in all cases really a question of the same reaction. Alcohol greatly accelerates denaturing at ordinary temperature, and the lyotropic series of ions, which may be investigated with protein sols as electrolyte-free as possible, takes similar effect as in the case of heat coagulation.[3] It is important, according to experiments by E. Herzfeld and Klinger [4] and Wiechowski,[5] that proteins also become insoluble by mechanical working, such as rubbing in a mortar, indeed, even by scraping off a glass plate. Wiechowski therefore recommends, in order to avoid this, that proteins be allowed to dry upon plates coated with difficultly fusible paraffin wax; they fall off from these after drying. Whether the change here is the same as in denaturing is not yet determined. Herzfeld and Klinger explain the phenomenon differently. They assume that the proteins in biological liquids, which are particularly concerned, are held in colloidal solution by degradation products, and that new surfaces are formed by rubbing which lack these substances and hence are difficult to peptize. Whether this is generally true may remain an open question. If this loss of solubility by mechanical influences should depend upon the same processes as denaturing, it would be comprehensible why proteins also become insoluble upon adsorption at interfaces. The reader may be reminded of the experiments of Ramsden on the loss of solubility at the surface towards gas (cf. p. 535) and of those of W. Biltz upon the loss of solubility on adsorption by Fe_2O_3. The micellæ closely packed in a surface layer are under similar conditions to those mechanically pressed together.

The Size, Shape, and State of Aggregation of the Micellæ of Hydrophilic Sols

We may say in retrospect that the micellæ of hydrophilic sols are mostly smaller than those of hydrophobic. The behaviour under the ultramicroscope does not alone, as often emphasized, permit of this conclusion; here it is possible that it is often only the slight difference in refractive index between micella and intermicellar liquid which is responsible for the fact that hydrophilic sols frequently cannot be optically resolved. But the far larger rate of diffusion is particularly strong evidence for the smaller size (cf. p. 546), as also are the results of molecular weight determinations by osmotic pressure (cf. p. 557). According to these, the size of the micellæ of hydrophilic sols usually lies between 1 and 10 $\mu\mu$, and the molecular weights are as low as 3,000 and under.

In respect of size, there is perhaps another point of distinction between hydrophilic and hydrophobic sols. It has already been shown on p. 399 how very varied are the sizes of the particles present in a hydrophobic

[1] Cf. e.g. *Pauli* and *Handovsky*, *loc. cit.* p. 611.
[2] Miss *Chick* and *C. J. Martin*, Kolloidchem. Beihefte **5**, 98 (1913).
[3] *Pauli* and *Handovsky*, *loc. cit.* p. 611.
[4] Biochem Zeitschr. **78**, 349 (1917).
[5] Biochem. Zeitschr. **81**, 278 (1917).

sol. We have, so to speak, an extended spectrum of size of particles. Upon this, of course, depends the difficulty of obtaining a mono-disperse mastic emulsion (cf. p. 344). As opposed to this, we have grounds for assuming that the solution molecules in a true solution, such as that of cane sugar, are, to a large extent, of the same size. We have as it were a spectrum with a single line. The fact that hydrophilic sols so clearly stand between hydrophobic sols and true solutions makes it probable that they are also in this respect more similar to true solutions. The spectrum of size of particle will be a line one, rather than a continuous one as in the case of hydrophobic sols. The case will often occur that two or more kinds of particles are present—such as the neutral protein particles and the protein ions in a protein sol—while particles of intermediate sizes are practically absent. The number of particles of various kinds will be to a large extent connected with the equilibria prevailing in the sol.

In the case of hydrophilic sols also a number of phenomena are known which point to a non-spherical, elongated form for the particles. This is true in the first place of soap solutions. They are as such at first generally optically empty; but in their jelly-like solidification, which will be considered more in detail later (p. 724), a mass of ultramicroscopically fine threads, crystals, or anisotropic amorphous solid particles, are formed.[1] In addition phenomena are observed which lead us to suppose that thread-like particles of the kind already exist in the sol. Thus Zsigmondy and Bachmann describe cases in which the threads appear suddenly in their full length, as if they had already been present in the sol in amicronic thickness and grew upon gelatinization to submicronic thickness. The formation of streaks has likewise frequently been noted in the case of soap solutions.[2] The same is true of that counterpart to the soaps, the cetylsulphonic acid investigated by Reychler[3] (cf. p. 569). Stream double refraction has also been observed in the case of soap solutions (cf. p. 546).

Relations are similar in the case of the protein fibrin, contained in blood; here also the thread-shaped particles were observed, not in the original sol, but very strongly and strikingly upon clotting (cf. p. 610). According to investigations by Hekma,[4] which follow older experiments, upon the coagulation of a fibrin sol under the ultramicroscope quantities of needle-shaped particles appear, the association, entanglement, and other behaviour of which recall point for point the behaviour of a vanadium pentoxide sol.[5] Also a brilliant shimmer, that is a formation of streaks, is observed, when this sol clots.[6] It is true that Stübel[7] prefers to regard this process as a simple crystallization. Since the fibrin does not give the X-ray photograph corresponding to a crystal (cf. p. 725), there are still certain objections to his view.

Closely allied, although perhaps of a somewhat different kind, are the anisotropic colloidal solutions of 10-bromophenanthrene-3 (or 6)-sulphonic acid in water discovered by Sandquist.[8] At sufficiently large concentration

[1] *Zsigmondy* and *Bachmann*, Kolloidzeitschr. **11,** 150 *et seq.* (1912).
[2] *Bunbury* and *H. E. Martin*, Journ. Chem. Soc. **105,** 420 and 425 (1914).
[3] Kolloidzeitschr. **12,** 278 (1913).
[4] Biochem. Zeitschr. **62,** 161 (1914); **63,** 158, 204 (1914); **64,** 86 (1914); **65,** 311 (1914); **73,** 370, 428 (1916); **74,** 63, 219 (1916); Internat. Zeitschr. f. phys.-chem. Biologie, **2,** 279, 299, 352 (1915).
[5] *Diesselhorst* and *Freundlich*, Internat. Zeitschr. f. phys.-chem. Biologie, **3,** 46 (1916).
[6] E.g. *Hekma*, Biochem. Zeitschr. **73,** 443 (1916).
[7] Pflüg. Archiv, **156,** 361 (1914); **181,** 285 (1920).
[8] Kolloidzeitschr. **19,** 113 (1916).

and low temperature these solutions behave like those colloidal electrolytes the second phase of which is an anisotropic liquid, such as anisotropic molten *p*-azoxyphenetole.

With other hydrophilic sols, in connexion with which such phenomena have not been described, the first assumption would be that their micellæ are approximately spherical.

As regards the state of aggregation of the micellæ, it follows, in any case, from these experiments, that they cannot be regarded throughout as liquid ; the lyophilic sols are not therefore all emulsoids. This is particularly true when the particles are not spherical, as probably in the case of solutions of the soaps and perhaps of cetylsulphonic acid. The case of fibrin sols is less conclusive ; here the micellæ of the original sol might be liquid, and only solidify on clotting. Why this assumption is improbable in the case of the soap sols has already been stated (p. 614). Among the sols which have been investigated most, such as those of starch, gelatine, proteins, etc., there is none the disperse phase of which separates in the form of a true liquid, as, for example, does benzene from a benzene emulsion. There are thus no cogent grounds for the supposition that the micellæ of hydrophilic sols are liquid. There is, perhaps, more to be said in favour of the view that imbibition, as observed in peptization, leads to a subdivision in which one micella consists of a framework of the amorphous solid or finely crystalline substance filled with water molecules, as it were a sub- or amicronic water-laden crystal or amorphous solid grain. This is true of large micellæ, not of such as hæmoglobin, which may be regarded as large molecules.

2. SPECIAL PART

Lyophilic Sols with Water as Dispersion Medium

The Hydrosols of Sulphur

The hydrosols of sulphur are particularly worthy of attention. They have often been referred to ; they will now be summarized and considered in detail. Odén [1] particularly has examined their behaviour in great detail in a comprehensive investigation ; the following account is taken from his results and from later investigations by P. Scholz.[2] In two respects these sols have led to an insight into fundamentals, or at least will do so. In the first place, they present a case in which one and the same substance forms the chief constituent of micellæ of different kinds of sols, not only of decidedly hydrophobic but also of sensibly hydrophilic ones. This allows an insight into the nature of hydrophilic sols. Secondly, in coagulation by electrolytes those influences of hydration appear particularly clearly which already made themselves evident in the case of the sulphide sols (p. 461).

As is well known, liquid sulphur appears in two forms : the yellow mobile S_λ preponderates between the melting-point (119°) and about 160°, above 160° the brown viscous $S\mu$ preponderates.[3] With slow cooling

[1] *loc. cit.* 368. There also a detailed bibliography.

[2] Not yet published.

[3] Concerning the behaviour of the various forms of sulphur see particularly : *A. Smith* and *W. B. Holmes*, Zeitschr. f. physik. Chemie, **42,** 473 (1903) ; *A. Smith, W. B. Holmes* and *Hall, ibid.* **52,** 602 (1905) ; *A. Smith* and *W. B. Holmes, ibid.* **54,** 257 (1906) ; *A. Smith* and *Carson, ibid.* **57,** 685 (1907) ; **61,** 200 (1908) ; *A. Smith* and *Brownlee, ibid.* **61,** 209 (1908) ; *A. Smith* and *Carson, ibid.* **77,** 661 (1911) ; *F. Hoffmann* and *R. Rothe, ibid.* **55,** 113 (1906).

$S\mu$ is transformed into S_λ, which latter crystallizes out as rhombic (or monoclinic as the case may be) sulphur. This form is readily and freely soluble in organic solvents, especially in carbon disulphide. But with quick cooling and in the presence of substances such as SO_2 and acids the sulphur heated above 160° solidifies to a tough amorphous solid (plastic sulphur). This dissolves much more slowly in organic solvents than S_λ. Smith regards plastic sulphur as a form containing $S\mu$ in the supercooled state. This does not appear to me to suffice to explain its properties. It remains unintelligible why SO_2 and acids favour its formation, and particularly, why ammonia entirely abolishes the conditions for its formation. Sulphur, when treated with NH_3 and strongly heated, gives, even upon rapid cooling, only S_λ, and the amorphous solid sulphur obtained by sudden cooling changes into S_λ at ordinary temperatures in the presence of aqueous solutions containing OH' ions. All these phenomena may be explained if we assume that polythionic acids, and particularly pentathionic acid $H_2S_5O_6$, are mixed with the supercooled $S\mu$, and that these greatly inhibit the transformation of plastic sulphur into S_λ in a manner not yet fully explained, and also influence its solubility in organic solvents. Pentathionic acid is formed by heating sulphur in the presence of water and hence can be formed under the conditions under which plastic sulphur is prepared; it is stable in presence of acids but unstable in the presence of ammonia and alkalis, which makes intelligible the conditions just described for the formation of plastic sulphur.

Now, among the sulphur sols there are both those with micellæ containing exclusively S_λ and those in which the micellæ probably consist to a considerable extent of amorphous sulphur. The Weimarn sulphur sol already frequently referred to is a sol containing S_λ sulphur.[1] It is prepared by dissolving rhombic sulphur in alcohol and pouring this solution into an excess of water. Pentathionic acid is not present in this sol, and the sulphur behaves throughout like S_λ, which should be the case according to the conditions of preparation. This sol, a milky, bluish-white liquid, is not very stable and, according to experiments of Scholz, is decidedly hydrophobic; small amounts of electrolyte suffice for coagulation, the F.V.s follow the rules given on p. 420 with regard to adsorbability and valency; the differences between the alkali kations are slight, the lyotropic series is therefore not well marked; $H^\cdot$ ions flocculate more strongly than the alkali kations. Upon coagulation with mixtures of electrolytes the kations to a large extent behave additively. The flocculated sulphur cannot be repeptized by water.

The behaviour of sols in which the sulphur has been formed by chemical reactions is very different. A considerable number of chemical reactions enable such sols to be prepared. Two of these have been particularly investigated. In the first place there is the reaction between SO_2 and H_2S, for which the formation of sulphur may be represented by an equation

$$SO_2 + 2H_2S = 3S + 2H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In reality a number of substances are formed, and the sulphur is produced exclusively or partially as a result of their further decomposition. Pentathionic acid[2] is also formed in large amount according to a gross equation

$$10SO_2 + 5H_2S = 3H_2S_5O_6 + 2H_2O.$$

[1] *loc. cit.* p. 427.

[2] As regards the chemical behaviour of the polythionic acids see particularly *Hertlein*, Zeitschr. f. physik. Chemie, **19**, 287 (1896); *Raschig*, Zeitschr. f. angew. Chemie, **24**, 290 (1911), and unpublished investigations of *Riesenfeld* and *Feld*.

Sols prepared according to equation (1) may be described as Selmi sols.[1]

A second reaction which gives sols is the decomposition of thiosulphate by acids according to the equation

$$Na_2S_2O_3 + 2HCl = S + SO_2 + 2NaCl + H_2O \quad . \quad . \quad . \quad (2)$$

Here, also, pentathionic acid is always formed, since the thiosulphuric acid at first liberated in part reacts further according to the equation

$$5H_2S_2O_3 = 2H_2S_5O_6 + 3H_2O.$$

This sol may be described as the Raffo sol.[2] Since the micellæ of the two sols have a very similar composition, it is convenient to describe both the Selmi and Raffo sols as Odén sols, since Odén has contributed most to their elucidation.

In both cases the sulphur remains dispersed in the liquid along with other reaction products. The foreign substances are removed as far as possible by coagulating the sulphur with NaCl, centrifuging, and repeptizing in pure water. Hence NaCl is usually present as an impurity in the sol.

In detail, Odén proceeds as follows. In the method represented by equation (1) H_2S is slowly led into a cold solution as concentrated as possible (e.g. 1·8 molar) of SO_2 in water: a small precipitate of difficultly peptizable sulphur at first formed is centrifuged off, the sulphur contained in the liquid is coagulated with a NaCl solution, filtered off, and the product peptized with pure water. In the case of reaction (2), a concentrated solution of sodium thiosulphate (about 3 N) is quickly mixed with concentrated H_2SO_4 (S.G. 1·84, about 18 N). Too large quantities must not be taken; only about 100 c.c. for each experiment. The liquid is cooled, the sulphur flocculated with NaCl, centrifuged, the supernatant liquid siphoned off, and the coagulated sulphur peptized with water at about 80°. Any difficultly peptizable sulphur present is centrifuged off.

The micellæ of the Odén sols contain, in the first place, amorphous sulphur, as is evident from the appearance and the solubility of the sulphur flocculated by NaCl. They further always contain, perhaps along with other foreign substances, pentathionic acid. This was detected as follows: Pentathionic acid reacts with alkalis and with ammonia with the formation of thiosulphate. In the warm, the process may be represented by the equation

$$2S_5O_6'' + 6OH' = 5S_2O_3'' + 3H_2O.$$

In the cold, it is more complicated; sulphites are formed in addition to thiosulphates. If the sulphur cake obtained by centrifuging sulphur sols, which have been so thoroughly purified that they only yield quite small quantities of substances which reduce iodine by simple washing with water or aqueous salt solutions, be treated with ammonia, the liquid standing over the sulphur consumes iodine freely after acidification; thiosulphate has been formed. The sulphur centrifuged off after treatment with ammonia gives upon further treatment with the latter no further quantity of iodine-reducing substance. Hence we are not dealing with an attack of ammonia upon sulphur. With Selmi sols 1 g. of sulphur generally binds 0·140 millimol of pentathionic acid, with Raffo sols about 0·450 milimol. The micellæ of these sols also contain much more water than do those of the more hydrophobic Weimarn sol. This follows from the mere fact that they are clearer and much more transparent than the hydrophobic sol.

[1] See *Odén*, "Der Kolloide Schwefel," p. 6.
[2] Kolloidzeitschr. **2**, 358 (1908).

Hence the micellæ of the Weimarn sol may be represented by a formula

$$\left[\begin{matrix} S_\lambda \\ H_2O \end{matrix}\right]' H^\cdot$$

—those of the Odén sols by

$$\left[\begin{matrix} S_\mu \\ S_5O_6H_2 \\ \underline{H_2O} \end{matrix}\right]' H^\cdot$$

It must remain unsettled for the present whether the latter do not also contain some S_λ, and further whether we are justified in assuming the $H^\cdot$ ion as mobile kation. The great stability of the Odén sols is, as we shall now see, caused by the large water content of the micellæ, and this evidently by the fact that the pentathionic acid has a strong affinity both for water and for sulphur. The S_5 group of the acid will tend to combine with the residual valencies of the sulphur molecules, the more so since sulphur forms molecules containing many atoms; residual valencies of oxygen atoms will, as in the carboxyl group and the like, have affinity for water (cf. p. 315).

The stability of the more hydrophilic Odén sols will now be compared with that of the more hydrophobic Weimarn sols. Both are shown by kataphoresis to be decidedly negatively charged. We have, therefore, even in the case of Odén sols, an influence of electrolytes (predominating effect of kations, of their adsorbability and valency) as in the case of hydrophobic sols. In agreement with this, as Odén proved, we have the fact that, as is usually the case in the coagulation of hydrophobic sols, the coagulating kations are to be found in the flocculated sulphur; whether it is here a matter of exchange adsorption has not yet been determined. But the relationships in the Odén sol are displaced in characteristic fashion by the special properties of the pentathionic acid and by hydration. Table 165 contains the F.V.'s of the two sols determined in the usual manner. The time of waiting before judging of settlement was extended to 18 hours, since sulphur, especially in these dilute sols, settles fairly slowly.

As regards the Weimarn sol, it has already been mentioned that it has a purely hydrophobic character. With the Odén sols, on the other hand, we have a series of divergences in the direction of a more strongly hydrophilic character. While bi- and tervalent and organic kations behave similarly in both sols, the alkali salts exert a surprisingly feeble coagulating action on the Odén sol. The lyotropic series is strongly marked. The acids, which otherwise flocculate throughout more strongly than the alkali kations, flocculate much more weakly.

These remarkable divergences may be explained by the pentathionic acid content of the micellæ. In acid solution this acid is particularly stable; on the other hand, the content of pentathionic acid conditions the stability of the micellæ. It is unnecessary to assume that all the pentathionate is originally present as acid, since in preparing the sols, solutions are always used which are rich in $Na^\cdot$ ions. The action of acids may therefore consist in the transformation of all the pentathionate into stable pentathionic acid, thus increasing the stability of the micellæ and therewith the F.V. of the sol.

Conversely, substances which lower the stability of or destroy pentathionic acid, should therefore decrease the stability of Odén sols, indepen-

TABLE 165

F.V.'s for a Weimarn and a Raffo Sulphur Sol

Electrolyte.	F.V. (millimol per litre) of a Weimarn Sulphur Sol (77 mg. S per litre).	F.V. (millimol per litre) of a Raffo Sulphur Sol (364 mg. S per litre).
$\frac{Li_2SO_4}{2}$	35	>1,500
LiCl	34	750
NaCl	33	190
KCl	32	85
RbCl	31	80
CsCl	30	95
$\frac{H_2SO_4}{2}$	10	900
HCl	10	850
NH_3	About 5,000	Chemical change
p-chloroaniline chloride	25	20
Strychnine nitrate	1·0	2·1
$Be(NO_3)_2$	2·3	1·0
$Mg(SO_4)$	4·2	1·6
$MgCl_2$	3·7	1·5
$CaCl_2$	3·8	1·5
$BaCl_2$	3·6	1·5
$AlCl_3$	—	0·05
$CeCl_3$	0·2	0·06

dently of the behaviour of such substances in the coagulation of hydrophobic sols. This is throughout the case. It has already been mentioned that alkalis react with pentathionic acid. In small concentrations they therefore destroy, as Odén already found, the Odén sols. The process appears to be different from ordinary coagulation. The originally yellowish sol becomes pure white and milky, and throws down non-repeptizable sulphur, which is now soluble in organic solvents. This is S_λ sulphur. If the Odén sol is originally taken sufficiently dilute, a sulphur sol may be made in this way which is similar to Weimarn's, the micellæ of which therefore contain essentially S_λ; a more hydrophilic sol has been changed by chemical means into a hydrophobic one, as is the case in the denaturing of a natural protein solution (see p. 609). As opposed to its behaviour towards Odén sols we have the large flocculation value of ammonia in the case of the Weimarn sol, in agreement with the behaviour of hydrophobic sols (cf. Table 112, p. 420).

Still more striking is the interaction with sulphuretted hydrogen. Pentathionic acid reacts with the latter according to the equation

$$H_2S_5O_6 + 5H_2S = 10S + 6H_2O.$$

Although the Odén sol is otherwise so stable towards acids, small concentrations of H_2S water coagulate it, or more correctly, transform it, as do alkalis, and alter its stability; the Weimarn sol on the other hand requires a larger concentration of the H_2S than of alkali salts for coagulation.

The special behaviour of the alkali metal kations doubtless depends

upon the fact that their pentathionates are comparatively stable, and may therefore be contained in the micellæ, and that they influence the water content of the micellæ favourably or unfavourably according to their hydration.

It has already been pointed out on p. 461 that the influence of hydration also appears particularly clearly in the case of flocculation by mixtures of electrolytes, and it is therefore met with still more strikingly with hydrophilic sols. In Tables 166 and 167 are given the results with a Weimarn and an Odén sol. With the hydrophobic sol all values lie under 100 per

TABLE 166

Influence of the Presence of other Electrolytes on the Coagulation of a Hydrophobic Weimarn Sulphur Sol

Content of Electrolyte first added in % of the F.V. in pure Solution.[1]	F.V. (in % of the F.V. in pure Solution) of the second Electrolyte added.[2]				
	KCl.	$MgCl_2$.	$CaCl_2$.	$BaCl_2$.	$CeCl_3$.
Electrolyte first added LiCl					
0	100 (31)	100 (3·7)	100 (3·8)	100 (3·6)	100 (0·20)
20 (7)	90 (28)	90 (3·3)	87 (3·3)	84 (3·0)	75 (0·15)
50 (17)	—	70 (2·6)	70 (2·6)	64 (2·3)	35 (0·07)
65 (22)	< 50 (< 16)	50 (1·8)	—	40 (1·5)	< 25 (< 0·05)
Electrolyte first added $\frac{H_2SO_4}{2}$					
32 (3·2)	< 64 (< 20)	60 (2·2)	66 (2·5)	61 (2·2)	—
50 (5·0)	< 50 (< 16)	54 (2·0)	40 (1·5)	55 (2·0)	—

TABLE 167

Influence of the Presence of other Electrolytes on the Coagulation of a Hydrophilic Selmi Sulphur Sol

Content of Electrolyte first added in % of the F.V. in pure Solution.	F.V. (in % of the F.V. in pure Solution) of the second Electrolyte added.			
	$MgCl_2$.	$BaCl_2$.	$AlCl_3$.	$CeCl_3$.
Electrolyte first added HCl				
0	100 (1·5)	100 (1·5)	100 (0·05)	100 (0·05)
4 (32)	180 (2·7)	60 (0·9)	60 (0·03)	60 (0·03)
20 (157)	660 (10)	95 (1·3)	300 (0·15)	80 (0·04)
50 (387)	1,000 (15)	285 (4·0)	1,260(0·63)	800 (0·4)
68 (533)	1,000 (15)	285 (4·0)	2,000(1·0)	1,000 (0·5)
Electrolyte first added $\frac{Li_2SO_4}{2}$				
About 35 (413)	2,000 (30)	235 (3·3)	3,200 (1·6)	8,000 (4·0)
„ 65 (763)	2,300 (35)	160 (2·2)	9,400 (4·7)	15,000 (7·5)
Electrolyte first added NaCl				
45 (87)	166 (2·5)	20 (0·3)	60 (0·03)	< 30 (< 0·015)
Electrolyte first added KCl				
30 (28)	130 (1·9)	60 (0·8)	80 (0·04)	55 (0·027)

[1] In brackets the concentration in millimols per litre.
[2] In the brackets the directly observed F.V. in millimols per litre.

cent.; with the hydrophilic, on the other hand, they rise to high multiples, in a much more striking manner than with As_2S_3 sols (see Table 124, p. 461). Here we have, even in a much greater degree than in the earlier case (p. 461), the antagonism of various kations, as is manifested still more decisively with biological electrolyte effects (see p. 469).

So much concerning the comparison of the hydrophobic Weimarn sol with the hydrophilic Odén sol and the insight thus obtained into the nature of hydrophilic sols. In the following, further properties of the hydrophilic S sols will be considered in connexion with Odén's investigations. The conditions of their stability here play a part, although in another direction. Odén mostly investigated a Raffo sol.

Odén sols may be prepared in very concentrated form; they contain up to 600 g. of sulphur per litre; they are then oily liquids, whose viscosity is several times that of water. The viscosity does not, however, increase very uniformly with increase in sulphur content, but only from a certain content onwards does the increase become rapid. The viscosity-sulphur content curve is therefore again (cf. p. 368) decidedly convex towards the axis of abscissæ. That this rise is stronger in the case of a sol containing chiefly amicronic, than with one containing chiefly submicronic particles, is important. This need not conflict with Einstein's law (cf. p. 367), according to which the viscosity should be independent of the dispersity of the disperse phase; for this law relates to sols with rigid particles large compared with the molecules of the dispersion medium and comparatively small in number: all conditions which are not fulfilled here. If the sulphur sols contain chiefly only amicronic particles, they are clear and yellow; the larger the particles become, the more turbid and milky do they appear.

It is not in contradiction with their hydrophilic behaviour that their surface tension hardly differs from that of water; for since molten sulphur at 250°, which is comparatively rich in S_μ, has a larger surface tension than water (118 dyne/cm.; cf. p. 77), and therefore all the more so at room temperature, no reason exists why the sulphur micellæ should lower the surface tension of water. It is only curious that the NaCl content of the sol, which amounted, for instance, with the more concentrated sols investigated to 3·3 per cent., with a sulphur content of 45 per cent., does not raise the tension; the σ of a 3·3 per cent. aqueous NaCl solution would be about 7 per cent. higher than that of pure water. This is doubtless to be explained by the greater part of the salt being adsorbed by the sulphur micellæ.

Density and refractive index increase to a great extent proportionally to the sulphur content.

In the foregoing discussion of the conditions of stability of these sols two circumstances have not been taken into account: the influence of the size of the particles, and the peptizability of the micellæ. Data have here been collected which extend much farther than is usual. It is still difficult to judge whether they only apply to these sols, or whether we may apply them to other hydrophilic sols generally, and assume that they have not been observed with other sols for the sole reason that only with the sulphur sols are various properties so fortunately combined. As particularly fortunate properties I should like to lay stress on the following:—The sulphur flocculated by many electrolytes (such as NaCl, etc.) may be entirely reversibly repeptized by water; if therefore the volume of the liquid is kept the same, after peptization the same number of ultramicro-

scopically countable particles are present as before. A sol with exclusively amicronic particles showed, after being coagulated and repeptized ten times, a light cone of the same appearance in the ultramicroscope. As a second peculiarity we have the fact already mentioned, that thanks to the great difference between the refractive indices of sulphur and water the sols can be to a large extent resolved ultramicroscopically, which with hydrophilic sols is seldom the case. These sols are also in so far similar to hydrophobic sols in that they are originally *polydisperse*, that is, contain particles of different sizes. Since we have the possibility of separating from them *monodisperse* sols, that is, sols which have particles of nearly equal size, the dependence of many properties upon the size of particle can be followed. In other cases this possibility is generally excluded: in the case of hydrophobic sols since, as a rule, monodisperse sols can only be prepared with difficulty, and with hydrophilic because the size of their particles is not known, and cannot be systematically altered. It is also a further peculiarity of these sols that they are much more concentrated than the hydrophobic sols otherwise investigated, and perhaps also than many hydrophilic.

Odén obtained monodisperse from polydisperse sols by fractional coagulation at constant temperature (room temperature). It appeared that amicronic particles require considerably greater amounts of electrolyte for flocculation than submicronic; thus a sol with particles of about $25\mu\mu$ diameter had a F.V., measured under definite conditions (coagulator allowed to drop in until a turbidity was produced), and with HCl as coagulator, of 1,850 millimols per litre, whilst one with particles of about $210\mu\mu$ had a F.V. of only 500 millimols per litre; on the other hand a completely amicronic sol had a F.V. of 4,800 millimols per litre. With NaCl as coagulator the corresponding values were 150, 70, and 300. Hence, if an amount of NaCl in concentration insufficient for complete coagulation is added to a polydisperse sol, and if this concentration is increased for successive coagulations, the first product contains the coarsest and the last the finest micellæ. The single fractions may be purified by peptizing them in NaCl solutions. Two limiting concentrations may thus be found, of which the higher coagulates practically completely; any finer particles present remain peptized and can be siphoned off. The smaller limiting concentration, on the other hand, peptizes the fraction completely. The monodisperse sols thus obtained show the required properties microscopically as well as ultramicroscopically. As far as they could be resolved, the particles were larger in the easily coagulable sol than in the difficultly; the colour showed a corresponding series of steps; the amicronic sols were light yellow and transparent, whilst the submicronic were turbid and milky, even in large dilution. NaCl is particularly valuable as coagulator, since the flocculation produced by it is practically always reversible.

The amount of NaCl adsorbed by the flocculated sulphur also depends greatly upon the size of the particles, a sign that we are obviously dealing with a surface phenomenon. The amount of NaCl adsorbed per gram of sulphur amounted, for instance, with an amicronic sol to 1·23 millimol, with a submicronic to only 0·48 millimol. Apparently the experimental conditions chosen by Odén were always within the range of adsorption saturation (cf. p. 182); for the amount adsorbed did not depend upon the NaCl content of the solution. A consequence of the dependence of the amount adsorbed upon the size of the particles is, that in a polydisperse sol the larger micellæ at first separating remove less NaCl from the solution

than the finer micellæ separating later. This was also confirmed by experiment.

It may be further expressly remarked that the regularities of Table 165, which according to the figures refer to an amicronic sol, are throughout maintained when we pass to submicronic sols.

Now between the flocculated sulphur and that remaining behind in the liquid well-defined equilibria are set up, which are readily reached from above and below, and which depend greatly upon the electrolyte concentration, the size of the particles, and the temperature, a phenomenon of a kind unique in colloid chemistry. Svedberg [1] was the first to investigate it more closely, after Debus [2] and Raffo [3] had already observed the ready peptization on warming. The coagulated micellæ have as it were a definite "solubility," or more correctly peptizability, for it differs from a true solubility in that it is in part a question of ultramicroscopically visible particles, and depends upon the size of the particles in quite a different manner from true solubility. With a monodisperse sol of a definite size of particle, the sulphur content S of the sol may be connected with the temperature by an equation

$$S = Ke^{t-t_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which K and t_0 are constants. How far the relation holds is shown by the following table.

TABLE 168

Temperature Equilibrium of a Mono-disperse Submicronic Sulphur Sol

NaCl content of the intermicellar liquid 0·101 molar. $K = 11{\cdot}11$; $t_0 = 14{\cdot}5°$

t in deg.	S (obs.) (g. S per 1,000 c.c. sol).	S (calc.).
10·0	0·1	0·1
11·5	0·5	0·5
14·9	15·3	16·7
17·0	140	135·4
17·5	222·3	223·2

If we compare this sol with one which is likewise monodisperse but with larger micellæ, t_0 and K are found to be larger, that is, at the same temperature the amount of sulphur peptized is smaller than with finer-grained sols. The lower branch of the steeper curve in Fig. 122 corresponds to the finer sol 1 ; the lower, less steep curve to the coarser sol 2. The curves end above in points which correspond to complete peptization of the flocculi ; they meet the axis of abscissæ below at a temperature which corresponds to complete flocculation.

If we have a sol containing particles of both sol 1 and sol 2,[4] then as in the upper curve an upper branch is attached to the lower. At first as the temperature rises the finer micellæ are peptized, and only then the coarser, so that a further increase of the sulphur content starts with a

[1] Kolloidzeitschr. **4**, 49 (1909).
[2] Lieb. Ann. **244**, 76 (1888).
[3] Kolloidzeitschr. **2**, 358 (1908).
[4] See *Odén*, "Der Kolloide Schwefel," p. 162 *et seq.*

singular point. It is easy to see that, when a sol contains very nearly equal amounts of particles of regularly graded sizes, the S, t curve passes over into a series of small arcs, that is, to a straight line. We have here, therefore, a new method of distinguishing a polydisperse from a monodisperse sol: with a monodisperse sol the lower curve holds, with a polydisperse sol a curve with many points is found, or eventually a straight line. These consequences were also confirmed by experiment.

An increase in electrolyte concentration acts similarly to an increase in the size of the particles. t_0—and in a lesser degree K—becomes larger; a higher temperature is therefore required with a higher electrolyte content in order to obtain the same sulphur concentration in the solution as with smaller salt content.

The large amounts of NaCl which were usually present in the sols investigated by Odén are not necessary for the stability of these sols. Odén was able to remove the electrolyte practically completely; he first displaced the NaCl by HCl and then electrolysed the sol in a tube in which the anode was separated by a collodion membrane from the interior of the vessel. The electrolytes passed into the anode chamber and were removed from time to time by replacing the liquid contained in the latter by pure water. As a result of kataphoresis the sulphur micellæ collected on the collodion membrane, and could finally be peptized by pure water to a stable sol. This only means that the NaCl and free HCl can be completely removed, but not, or not completely, the pentathionic acid, which is contained in the micellæ. Since this, as active electrolyte, is necessary for the stability of the sol, one can understand why the micellæ in question could be repeptized.

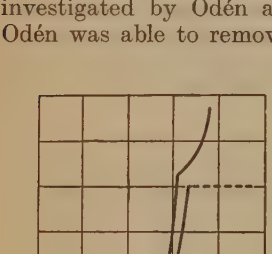


Fig. 122.—Dependence of the Peptizability of the Sulphur Micellæ upon the Temperature and Size of Particles.

It is not yet evident from the foregoing investigations how far the nature of the various ions influences the peptizability of the separated micellæ. In general, the flocculation of Odén sols is reversible when the electrolyte—with the exception of the alkalis and salts with an alkaline reaction—does not act for too long a time and in too great a concentration; especially with strongly coagulating salts with multivalent kations a part of the flocculated sulphur is soon incapable of being repeptized. This can be partly explained in the manner given on p. 472. The sulphur drops at first only adhere without coalescing. In course of time, however, coalescence occurs more and more, and in this coarsening circumstances similar to those concerned in coagulation itself play a part (cf. p. 455); finally the transformation $S_\mu \longrightarrow S_\lambda$ gradually takes place. Sulphur crystals are, in fact, always found in old sulphur sols,[1] and a reversal of adsorption has been followed on flocculated sulphur (cf. p. 453). Quite similar facts are true of the flocculation and peptization of hydroxide sols (cf. p. 471).

Probably, however, the pentathionic acid content is decisive for peptizability, and that depends further upon the greater or smaller stability of the salts of the polythionic acids. That an irreversible flocculation always

[1] *Odén*, "Der Kolloide Schwefel," p. 173 *et seq.*

occurs in the presence of an excess of OH' ions, and likewise under the action of H_2S, depends of course upon a destruction of the pentathionic acid (cf. p. 619).

The coarsening of the sulphur flocculi and their gradual crystallization and therewith the reversal of adsorption depend greatly upon the temperature. They therefore take place slowly at low temperatures; hence peptization can be carried out at low temperatures under conditions under which this is impossible at higher temperatures. It thus comes about, that the micellæ of Odén sols readily repeptize upon freezing and thawing.[1]

The micellæ of sulphur sols are chemically very reactive. Of the many reactions described by Raffo,[2] attention may be drawn to those with silver nitrate and silver sulphate solutions in which silver sulphide is formed. The easy formation of heavy metal sulphides makes it intelligible that Odén [3] was able to form sols of the sulphides of noble metals by the action of sulphur sols upon solutions of salts of noble metals; besides silver salts solutions of gold chloride and chloroplatinic acid were investigated. The curious interaction of the Odén sol with As_2S_3, Se, and Ag sols, and the part probably played therein by pentathionic acid, has been described earlier (pp. 477 and 488).

Hydrophilic Sols of Oxides and Hydroxides

According to their chemical nature these sols are so closely connected with the "hydrophobic" sols of metallic oxides and hydroxides dealt with above (p. 519), that it may appear arbitrary to consider them separately here. But their conditions of stability are different in so many respects, that I regard this separation as justifiable. The hydroxides which belong to this group are almost entirely of an acid character, and the elements the oxides and hydroxides of which come into question are frequently metalloids, or more nearly allied to them than the elements, the oxides and hydroxides of which give sols of a hydrophobic character.

The Silicic Acid Sols

We have first the sol of silicic acid, which was exhaustively investigated by Thomas Graham.[4] It is obtained essentially by condensation methods; the silicic acid is liberated from its salts in solution by hydrochloric acid and the sol purified by dialysis, or a suitable volatile silicon compound, silicon chloride or the ethyl ester of silicic acid, $Si(OC_2H_5)_4$,[5] is hydrolytically decomposed by water and this solution then dialysed. The method of Ebler and Fellner [6] appears to be very clean and free from objection. The vapour of silicon chloride is passed into water, and the solution dialysed, and evaporated. It is not true that considerable amounts of electrolyte are necessary for the permanence of the sols. Zsigmondy [7] was able, by effective dialysis, to free a sol prepared by the action of HCl upon a solution of waterglass practically completely from electrolytes; small residues

[1] *Odén*, "Der Kolloide Schwefel," p. 67.
[2] *Raffo* and *Pieroni*, Kolloidzeitschr. **7**, 158 (1910).
[3] "Der Kolloide Schwefel," pp. 184–5.
[4] Lieb. Ann. **121**, 36 (1862), **135**, 65 (1865); Pogg. Ann. **123**, 529 (1864).
[5] *Grimaux*, Compt. rend. **98**, 1437 (1884).
[6] Ber. d. deutsch. chem. Ges. **44**, 1915 (1911).
[7] *Zsigmondy* and *Heyer*, Zeitschr. f. anorg. Chemie, **68**, 169 (1910).

of Na_2SO_4 present as impurities were difficult to remove. In the preparation it is advantageous for the acid to be in excess; hence the waterglass solution (about 10 per cent.) is poured into the 10 per cent. HCl.[1]

A phenomenon which is also perceptible, although to a very much smaller degree, in the case of other hydroxide sols, is very marked with silicic acid sols. The silicic acid, freshly separated from the silicate, is not colloidal, but is present in true solution; it diffuses rapidly through membranes and lowers the freezing-point considerably, as was first observed by Mylius and Groschuff.[2] From the start the particles of the silicic acid rapidly become coarser, the process being accelerated, according to the statements of the investigators named, by the silicate present; they diffuse first more slowly and finally not at all through membranes; the depression of the freezing-point becomes smaller. This transformation may also be followed by the fact that the original crystalloidal solution of silicic acid is unable to flocculate protein sols, while the solution as it becomes progressively more colloidal gains this property to an increasing extent. Upon what this process depends—whether it is rather a matter of polysilicic acids, which give larger micellæ, being formed from the simple silicic acid; or whether the crystalloid particles originally present already consist of polysilicic acids, but are exceedingly fine amicrons, which continually increase in size; or finally whether a hydration is more important than the polymerization, or whether all these processes or several of them take place together—cannot yet be said with certainty.

In any case it is this process which also mainly conditions the further stability of the silicic acid sol. Upon it doubtless depends the fact that for these sols, in a more prominent manner than for others, an upper limit of the concentration exists which can only be exceeded with difficulty. Graham [3] described a sol containing 140 g. per litre, which, however, set in a short time to a jelly. Zsigmondy [4] did not succeed in preparing sols containing more than 120 g. per litre. Sols in which about 10 g. per litre are present keep for years, according to his statements. But from all accounts one gets the impression that even with such dilute sols it would be possible by means of a suitable reagent to detect a continuous change in the same direction. Thus Garrett [5] found that the viscosity of silicic acid sols increases continuously in course of long periods of time.

According to experiments by Pappadà,[6] the sensitivity towards electrolytes is, in general, slight. A rapid flocculation or formation of a gel, as in the case of an aluminium hydroxide sol, is not observed with salts of the alkalis or alkaline earths; the gelatinization is certainly accelerated, but it still takes place comparatively slowly, e.g. in a molar solution of $CsNO_3$, a comparatively active salt, in about 20 hours. This in fact tells against one of the possibilities mentioned above, namely, that the coarsening of the micellæ is colloido-chemical in nature, as in the earlier case of the Fe_2O_3 sols (cf. p. 455) or of reversal of adsorption (p. 453); a more chemical

[1] *Kieseritzky* ["Die Gerinnung des Faserstoffs, Alkalialbuminats und Azidalbumins verglichen mit der Gerinnung der Kieselsäure." Diss., Dorpat, 1882] believes that he increased the stability of SiO_2 sols by adding HCl to them during dialysis, and thus preventing the sol from being depleted of acid too quickly, owing to the rapid dialysis of the HCl.

[2] Ber d. deutsch. chem. Ges. **39**, 116 (1906).

[3] Lieb. Ann. **121**, 37 (1862).

[4] "Kolloidchemie," 3 Aufl., p. 211.

[5] *loc. cit.* p. 539.

[6] Gazz. chim. ital. **33**, II, 272 (1903); 35, I, 78 (1905).

polymerization and hydration is likelier. That, according to Pappadâ, the lyotropic series of the kations again becomes very prominent, in the acceleration of gel-formation by alkali salts, as in the case of sulphur and negative hydroxide sols (cf. p. 427), would agree with a considerable influence of hydration. Lithium salts accelerate least, cæsium most strongly.

It also behaves differently from a hydrophobic sol towards alkalis. Since the particles of a silicic acid sol are negatively charged in faintly alkaline, neutral, and faintly acid solution, one would have expected that OH' ions would charge up and increase the stability. The opposite is the case. Even after addition of a little alkali the sol appears more turbid; if an alkali salt is then added, strong flocculation or complete gelatinization occurs instantaneously, while, without the addition of free alkali and with the same alkali ion concentration the sol remains completely unaltered for a long time. At higher OH' ion concentrations this favourable influence of alkali upon gelatinization is less marked; there appears to be an optimum of the effect at a certain small OH' ion concentration. The statements of Fleming [1]—who worked with undialysed sols containing NaCl, and followed the velocity of gelatinization under the influence of various H' and OH' ion concentrations, and found a maximum of the velocity with a certain small excess of OH' ions—are thus explained. Whether this sensitization by OH' ions or alkali silicate is to be brought into relation with the sensitization discussed earlier (p. 583), is questionable; perhaps it is rather connected with the observation of Mylius and Groschuff, that alkali silicates cause or favour the transformation of the crystalloid silicic acid into the colloid.

In some respects we are reminded of an influence of the negative charge upon the stability, as when aluminium sulphate (it is true in comparatively large concentrations) and salts rapidly coagulate basic dyes. That sols of proteins, glue, and others do so, will scarcely be regarded as a coagulation of oppositely charged sols (cf. p. 477); rather perhaps as the formation of difficultly soluble, jelly-like silicates of the proteins in question or as a sensitization in the sense of the sensitization of Fe_2O_3 sols by albumin, and similar processes (see p. 583).

Silicic acid sols appear to be curiously sensitive towards solid powders. Graham [2] caused a 5 per cent. sol to gelatinize in a few hours by adding powdered graphite.

The gelatinous or flocculent silicic acid cannot be repeptized in water or acid solutions. This, however, succeeds with alkalis. The action of aqueous, fairly concentrated NH_3 solution has been investigated by R. Schwarz.[3] The following result was obtained. First of all a peptization of the silicic acid occurs; with longer duration of the action more and more colloidal silicic acid is truly dissolved. The change in the conductivity shows the presence of silicate ions. With increase in age of the silicic acid gel the rate of dissolution decreases greatly. Here also Schwarz and Liede [4] found *a* and *b* forms of silicic acid, as will be discussed in the case of the stannic acids (p. 632).

In the case of silicic acid the heat change upon coagulation has also been measured. Wiedemann and Lüdeking [5] coagulated silicic acid, freshly set

[1] Zeitschr. f. physik. Chemie, **41**, 443 (1902).
[2] Lieb. Ann. **135**, 67, 1865.
[3] Ber. d. deutsch. chem. Ges. **49**, 2358 (1916); **52**, 601 (1919); *R. Schwarz* and *Souard*, *ibid.* **53**, 1 (1920); *R. Schwarz* and *Liede*, *ibid.* **53**, 1509 (1920); *R. Schwarz*, Kolloidzeitschr. **28**, 77 (1921).
[4] Ber. d. deutsch. chem. Ges. **53**, 1680 (1920).
[5] Wied. Ann. **25**, 145 (1885).

free from waterglass solution by HCl, with ammonia, and found values of + 11·3 and 12·2 gram-calories per gram of SiO_2. Doerinckel[1] also found several gm.-cals. per g. SiO_2. The development of heat is thus certainly greater than with hydrophobic sols (see p. 467).

From silicic acid sols crystals of quartz and tridymite may also be obtained, just as sulphur crystals are obtained from sulphur sols. But the process proceeds much more slowly; such crystals have only been obtained by heating sols in sealed tubes for weeks or months at temperatures of 250° and over.[2]

Silicic acid sols are to a great extent optically empty under the ultramicroscope.

Stannic Acid Sols

Stannic acid sols have a certain similarity to silicic acid sols and yet a very decided character of their own. Colloidal stannic acid solutions may be obtained by liberating the stannic acid from an aqueous stannate solution by hydrochloric acid and dialysing.[3] The reverse way may also be taken. The stannic acid is liberated by pouring dilute stannic chloride solution into dilute ammonia and dialysing.[4] In contradistinction to silicic acid a separated gel of stannic acid can usually be easily repeptized. Hence a sol may also be prepared by hydrolysing a stannic chloride solution with much water and peptizing after washing out.[5] Mecklenburg[6] uses, instead of stannic chloride solutions, solutions of stannic sulphate in concentrated sulphuric acid, which is allowed to drop into excess of water and so hydrolyse. The separated hydroxide is again washed and peptized. One may also obtain the hydroxide with Zsigmondy[7] by passing air through a dilute $SnCl_2$ solution, decanting until the chlorine reaction disappears, and peptizing with ammonia. Both alkalis and ammonia are suitable peptizing agents, as also are hydrochloric acid and oxalic acid; the amphoteric nature of the stannic acid thus appears. The sols prepared with alkali are negative, those with acid positive.

Negative stannic acid sols differ so little from the electrocratic hydroxide sols already considered, that we are perhaps hardly justified in separating them. A certain quantity of alkali is necessary to peptize a certain amount of stannic acid gel; according to Zsigmondy and Heinz[8] potassium hydroxide is a better peptizing agent than sodium hydroxide. It depends upon the nature of the gel to be peptized what amount of alkali is just sufficient for peptization. In one example it amounted to 0·033 millimol K_2O to 1 g. SnO_2; in another only 0·0066 millimol K_2O to 1 g. SnO_2. In both cases heating was long continued. The amount of peptizing agent was changed systematically up to a ratio of 3·3 millimol K_2O to 1 g. SnO_2.

It was with stannic acid as example that Zsigmondy[9] was first able so

[1] *loc. cit.* p. 467.

[2] *de Senarmont*, Ann. d. chim. et d. phys. (3), **32**, 129 (1851); *v. Chrustschoff*, N. Jahrb. d. Mineral. **1**, 205 (1887); *Bruhns, ibid.* **2**, 62 (1899).

[3] *Th. Graham*, Pogg. Ann. **123**, 538 (1864).

[4] *E. A. Schneider*, Zeitschr. f. anorg. Chemie, **5**, 82 (1894).

[5] *Zsigmondy*, Lieb. Ann. **301**, 370 (1898).

[6] Zeitschr. f. anorg. Chemie, **74**, 207 (1912).

[7] Lieb. Ann. **301**, 369 (1898).

[8] *Heinz*, "Über Kolloide Zinnsäuren wechselnden Alkaligehaltes." Diss., Göttingen, 1914.

[9] *Heinz, loc. cit.*; *Zsigmondy*, Zeitschr. f. anorg. Chemie, **89**, 210 (1914).

clearly to develop his explanation of peptization. Alkali forms stannate, K_2SnO_3. The stannate ion SnO_3'' is probably adsorbed strongly by the stannic acid or forms, if we prefer this point of view, molecular complexes with SnO_2 and H_2O in the sense of Werner's theory. If the graphic representation proposed by Zsigmondy and mentioned above (p. 391) be made use of, the micellæ of alkali stannic acid sols may be represented in the following manner :—

$$\left[\begin{matrix}SnO_2\\H_2O\end{matrix}\right]SnO_3''(K')_2$$

The double or multiple particles, which compose the gel to be peptized, become charged, their adherence to one another is diminished or abolished, and they are distributed through the liquid in consequence of the Brownian movement. The more peptizing agent one adds, the further proceeds the subdivision of the multiple particles into micellæ composed of fewer particles, and finally into simple single micellæ, which can no longer, or only very slowly, be further changed and diminished in size. This view is supported by the fact that when sols with but little peptizing agent are ultra-filtered through collodion membranes, the stannic acid almost completely remains behind on the filter—the particles are therefore large—while with increasing amounts of peptizing agent more and more stannic acid goes through the filter. Under the ultramicroscope the sols with little peptizing agent show a strong cone of light, in the case of those with more peptizing agent the cone becomes more and more indistinct, and finally disappears completely. The growth of the osmotic pressure of sols with increasing amounts of peptizing agent can be explained in the same way.

How sensitive is the amount of alkali required for peptization to small changes in the stannic acid gel, is evident from the following experiments.[1] The pressing together of the micellæ of a sol during ultrafiltration, indeed, even simple filtering upon paper, is sufficient to increase greatly the amount of alkali required for peptization. A gel that could originally be peptized with 0·0066 millimol K_2O per 1 g. SnO_2 required after filtering on a filter paper 0·165 millimol K_2O ; after strong suction in a collodion filter as much as 0·33 millimol.

Flocculation by electrolytes is in so far similar to that of hydrophobic sols, in that the nature of the kation plainly preponderates. But the influence of valency is greatly diminished. It is true that the kations of the alkali metals act comparatively weakly and require larger concentrations than the multivalent kations and H' ions, but these act, with fair accuracy, equally strongly in equivalent amounts. Such behaviour is not necessarily in contradiction to the adsorption theory of coagulation. For if the adsorption does not take place according to the ordinary isothermal, but according to Henry's law—which frequently happens, and especially in the case of hydroxides (cf. p. 191)—such behaviour must occur if, as earlier assumed (p. 422), the kations are practically equally adsorbed in equimolecular concentration. It has unfortunately not yet been tested whether the adsorption isothermal for stannic acid micellæ is, in accordance with Henry's law, a straight line passing through the origin. That the strongly

[1] Experiments by *Zsigmondy* and *Glixelli*, see *Zsigmondy*, "Kolloidchemie," 3rd Ed., p. 245 *et seq.*

acting kations, $H^{\cdot}$ ions and the multivalent ones, pass into the flocculi, has been proved.

As with negative hydroxide sols of Mo_2O_5 and V_2O_5 (see p. 471), the flocculi coagulated by the feebly acting alkali kations may be readily repeptized by washing out with water, while this does not succeed with the strongly acting kations such as $H^{\cdot}$ and multivalent ions.

The concentration of electrolyte necessary for flocculation lies in general somewhat higher than is usual with hydrophobic sols. It is approximately equivalent to the amount of KOH used for peptization. This means that either the whole amount of added alkali goes on to the micellæ as charging active electrolyte, or at any rate always the same fraction.

An investigation of the conductivity of these sols by Varga [1] agrees well with these results. He measured both the conductivity of the sols themselves and that of the intermicellar liquid obtained by ultrafiltration, from which the conductivity of the micellæ could be obtained by difference. The first small amounts of alkali added to the stannic acid gel only cause the formation of a suspension, which settles rapidly. At first the conductivity only increases very slightly, the alkali stannate formed is therefore bound to the micellæ in such a manner that, practically, it does not come into question for the transport of electricity. Only with larger amounts of alkali, when the gel is peptized to a stable sol with many small micellæ, does the conductivity increase greatly, both that of the intermicellar liquid, and also especially that of the micellæ; these therefore take a large part in the conductivity, just as in the case of soap solutions. Since the amount of electrolyte added for coagulation is approximately equivalent to the total amount of alkali added, it follows that the kation of the stannate enters completely into exchange with the kation of the added electrolyte, but that on the other hand the kations situated more in the interior of the micellæ do not take part in the conduction of electricity. This agrees with the results of Whitney and Ober [2] that the kations bound to coagulated As_2S_3 flocculi are completely exchanged on treatment with another electrolyte. It was not, a priori, improbable that the kations contained in the coagulated flocculi would only participate to a small extent in the conduction of electricity.

In the peptization of stannic acid gels with HCl [3] much higher concentrations are necessary than with alkali; for 1 g. SnO_2 about 26·5 to 132 millimol HCl; or for 1 mol SnO_2, 4 to 20 mol HCl. Although the amount of HCl is greater than would be necessary to change the Sn completely into $SnCl_4$, but little tetrachloride is formed by the action in the cold; a great part of the tin is in colloidal solution: it is retained by the ultrafilter and shows properties which depend on those of the original gel and the peptizing agent. We are dealing with electrolyte solutions containing colloid particles; stannic acid sols of this kind doubtless belong to a group of hydrophilic sols, further examples of which (e.g. solutions of viscose) will be mentioned later (cf. p. 639); with these, considerable concentrations of electrolyte must be present for the micellæ to remain peptized at all. The positive nature of these colloidal solutions is evident from the fact that they are flocculated by sulphates, and also by HCl in much higher

[1] Kolloidchem. Beihefte **11**, 3 (1919).

[2] *loc. cit.* p. 427.

[3] *R. Franz*, "Beiträge zur Chemie der Zinnsäure vom kolloidchemischen Standpunkt aus." Diss., Göttingen, 1913.

concentration. The coagulation by other anions has apparently not yet been examined. In contrast to the stable alkali sols, the hydrochloric acid sols are unstable, undergo continual changes, and are coagulated by heat.

The diversity of the phenomena with stannic acid sols is increased by the fact that perhaps to a more pronounced degree than with the sulphur sols *single particles*, *primary particles* or *particles of the first order* of quite different kinds may occur according to the conditions under which the gel to be peptized had been obtained, and that these particles retain their properties in colloidal solution comparatively unaltered under various kinds of treatment. Mecklenburg [1] was the first to investigate these phenomena more closely and to recognize their manifold importance. He prepared the various kinds of primary particles as follows. A solution of stannic sulphate in sulphuric acid was hydrolysed by being allowed to flow into water; the water had various temperatures, 0°, 25°, 50°, 75°, and 100°. The amount of water was not so great that under the conditions of experiment stannic acid separated immediately: this only happened at the temperatures above 50°. The aqueous solution first obtained was always diluted with an equal volume of water in order to precipitate the stannic acid. The acids obtained differed, after washing and drying, even in external appearance; that obtained at 0° was almost transparent, that at 100° like starch and opaque; the others were intermediate in appearance. Corresponding with this, the water content was also very different; with the 0° preparation, about 32 millimols of water to 1 g. SnO_2, with the 100° preparation 5·96 millimols H_2O to 1 g. SnO_2.

Now everything is in favour of the view that, corresponding to the larger adsorptive power for water, the 0° preparation consists of smaller particles of the first order than the 100° preparation. This shows itself in the first place in the power of adsorbing phosphoric acid; calculated on the gram of SnO_2, the 0° preparation adsorbs more phosphoric acid than the 100° preparation; at a concentration of about 40 millimol P_2O_5 per litre, 0·68 millimols of P_2O_5 are adsorbed by 1 g. of SnO_2 prepared at 0°, 0·25 millimol P_2O_5 by 1 g. SnO_2 prepared at 100°. Since the adsorption isothermals are affine (see p. 186), it follows that the chemical nature of the particles is the same, and that they only differ in the size of their surface, and hence that the particles are of different sizes. Similar facts are true of the adsorption of potassium ferrocyanide. Upon peptization, the gels prepared at lower temperatures may be dissolved by HCl to clear stable sols; this is quite impossible with the 100° preparation. The concentration of Na_2SO_4 required to flocculate these sols is, on the other hand, under comparable conditions, higher for the sols from low-temperature preparations than from high. The small particles of the gels made at lower temperatures are also more readily attacked chemically than those prepared at higher temperatures; thus in the same time more $SnCl_4$ is formed by HCl with the former than with the latter.

Now Mecklenburg [2] was able to show that the complicated group of phenomena, which is summarized in analytical chemistry as the isomerism of the stannic acids, is to be referred to the fact that under chosen experimental conditions SnO_2 sols are obtained with different kinds of primary particles differing from one another as do those prepared at different tem-

[1] *loc. cit.* p. 628.

[2] *loc. cit.* p. 628; further, Zeitschr. f. anorg. Chemie, **64**, 368 (1909); **84**, 121 (1913).

peratures in the experiments just discussed. The so-called *a*-stannic acids contain particles of the first order, which correspond in their properties to the primary particles obtained in the cold; they are formed in the cold by the interaction of crystalloids—$SnCl_4$ with alkali or stannate with acids—and may be readily peptized by acids. The so-called *b*-stannic acids or meta-stannic acids arise from the *a*-stannic acids by ageing or heat, that is, by accelerated ageing. Their particles of the first order correspond to the primary particles prepared by Mecklenburg in hot solutions; indeed, his preparation obtained at 100° shows the properties of a *b*-acid even more markedly than the *b*-acids of analytical chemistry. It is insoluble in concentrated HCl, and only soluble on dilution with water; it is very easily coagulated in the cold by sulphates. The only reaction which apparently gives the *b*-acid directly is the dissolution of metallic tin in nitric acid containing HCl. According to observations by R. Weber[1] and others, however, a clear SnO_2 solution—*a*-acid peptized in nitric acid—is first obtained with careful cooling, and this only deposits the insoluble *b*-acid upon warming. The ageing of the micellæ, which proceeds rapidly with silicic acid (see p. 626), apparently goes so slowly with stannic acid, that sols of different types with particles in different stages of ageing may apparently be kept unchanged for considerable lengths of time.

The description of the behaviour of a stannic acid sol is therefore incomplete when it is not stated with what particles of the first order we are dealing. The phenomena above described in connexion with alkaline and acid peptization relate essentially to an acid which approaches the *b*-stannic acid. In general it may be said that the behaviour of the SnO_2 sols becomes more hydrophobic, the more the micellæ have the character of those of the *b*-acid.

But a stannic acid sol cannot be characterized alone by the primary particles.[2] Clear or turbid appearance, behaviour under the ultramicroscope, flocculation value, reversible behaviour in flocculation with alkali salts, etc., do not depend solely upon the nature of the particles of the first order, but also upon those of the *second* and *higher orders*: that is, those consisting of several single particles. These are present in greater or smaller number, and with different properties, according to the previous history of the sol to be peptized, and the nature and effect of the peptizing agent. The appearance of the sol especially depends in a very complicated manner upon the particles of higher order.

Zocher[3] rightly draws attention to the following. In passing down the vertical column of the periodic table from silicon through tin to lead, the metals become progressively more electropositive, while the affinity for water progressively decreases. Corresponding with this, silicic acid forms the most distinctly hydrophilic sol of any inorganic substance. With stannic acid, a more hydrophobic behaviour is plainly marked, and the sols of plumbic acid are apparently purely hydrophobic. Bellucci and Parravano[4] prepared them as brown sols by hydrolysis of the salt $Pb(OH)_6K_2$, and found them especially sensitive towards kations, in accordance with the rules holding for hydrophobic sols.

[1] Pogg. Ann. **122**, 365 (1864).
[2] *Mecklenburg*, Zeitschr. f. anorg. Chemie, **74**, 239 *et seq.* (1912).
[3] "Über zinnsaure und bleisaure Salze." Diss., Berlin, 1920.
[4] *loc. cit.* p. 374; further, Gazz. chim. ital. **37**, I, 171 (1907).

Other hydrophilic Hydroxide Sols

In discussing the "hydrophobic" hydroxide sols (cf. p. 522), it was already emphasized that two kinds of sols can frequently be distinguished: water-clear ones, mainly obtained by hydrolysis and dialysis; and milky, turbid ones obtained mostly by peptizing flocculated hydroxides. Probably the same differences exist between them as between *a*- and *b*-stannic acid sols. A systematic comparison of two such sols has not yet been carried out on a comprehensive scale. Some experiments in this direction were undertaken by Kohlschütter and Frei [1] on *thorium oxide sols*. They obtained a water-clear sol by A. Muller's method,[2] by peptizing freshly precipitated $Th(OH)_4$, after washing, by heating with dilute HCl; and a turbid sol by bringing into colloidal solution with HCl a ThO_2 prepared by careful ignition (at 500°–600°, not over 800°) of thorium oxalate. With some electrolytes the flocculation values of the clear sol were in fact higher than those of the milky one. The flakes coagulated from the clear sol by sulphuric acid readily redissolve in the latter, evidently with formation of thorium sulphate, while this is not the case with the flakes from milky sols. The hydrophilic nature of the clear sol also follows from the fact that when dried it forms a gummy mass, which swells in water; with the viscous liquid thus obtained paper can be stuck together, as with gum arabic.

Quite similar are the differences between the clear *zirconium oxide sol*, prepared by dialysis of a solution of zirconium nitrate [3] or zirconium oxychloride,[4] and the turbid sol which can be prepared from the clear one by boiling. Corresponding results are to be expected with titanic acid sols. Th. Graham [5] prepared them by precipitating titanium salts with ammonia, peptizing the precipitate with hydrochloric acid, and dialysing. That the ageing of V_2O_5 sols, as seen in the gradual appearance of double refraction and formation of streaks (cf. p. 408), has the same cause as the changes just described in silicic acid, stannic acid, and zirconium oxide sols is possible, but not certain. Against it is the fact that with V_2O_5 sols a gradual diminution of the double refraction can be produced by diluting the sol; this rather points to slow flocculation as a cause of ageing. The investigations of *chromic hydroxide sols* [6] do not suffice to decide whether the sol mostly prepared by hydrolysis of the salts is more like Fe_2O_3 and Al_2O_3 sols, or the more hydrophilic sols.

With some other hydroxide sols, such as those of *molybdic* and *tungstic acids*, the forms with very small particles appear to be produced preferentially or perhaps, more correctly, ageing takes place comparatively slowly. They thus belong to the group of sols to which the soaps, dextrins, many dyes, and other substances belong, which are decidedly hydrophilic and form the transition to true solutions (with molecular weights of some thousands). Th. Graham [7] obtained the sols in question from sodium molybdate and tungstate solutions respectively, by acidifying with HCl. The molybdic acid sols were yellow, the tungstic acid sols colourless, and both were apparently quite insen-

[1] Zeitschr. f. Elektrochemie, **22**, 145 (1916).
[2] Kolloidzeitschr. **2**, suppl. 1, p. vi, 1907.
[3] *W. Biltz, loc. cit.* p. 520.
[4] *Ruer*, Zeitschr. f. anorg. Chemie, **43**, 282 (1905).
[5] Lieb. Ann. **135**, 77 (1865).
[6] *Th. Graham*, Lieb. Ann. **121**, 52 (1862); *W. Biltz*, Ber. d. deutsch. chem. Ges. **35**, 4431 (1902); **37**, 1095 (1904); *H. W. Fischer* and *Herz*, Zeitschr. f. anorg. Chemie, **31**, 352 (1902); *H. W. Fischer, ibid.* **40**, 39 (1904); *Neidle* and *Barab*, Journ. Amer. Chem. Soc. **38**, 1961 (1916); **39**, 71 (1917).
[7] Lieb. Ann. **135**, 77 *et seq.* (1865).

sitive to electrolytes; when dried they left behind gum-like masses which could be repeptized. Later investigators [1] were not apparently dealing with the same sols as Graham. Sometimes the alkali content appeared with them to be greater, sometimes the sols they investigated diffused more easily through membranes than Graham's. Thus, according to the work of Rosenheim and his co-workers,[2] the dihydrate of molybdenum trioxide, $MoO_3 + 2H_2O$, goes into solution with a definite solubility. The dissolved substance diffuses through parchment paper, the solution conducts well, the freezing-point method gives molecular weights of about 600. Since the dissolved substance is strongly dissociated, the molecular weight of the compound must be higher than this; Rosenheim and Bertheim assume an octomolybdic acid ($Mo_8O_5H_2$) with a molecular weight of about 1,170. Some properties recall those of colloidal solutions. Thus molybdic acid solutions have a strong tendency to supersaturation, a characteristic which is frequently met with in semi-colloidal solutions [3]; further, upon evaporating the solution over sulphuric acid below 20° a glassy residue is obtained, which can be peptized to a sol coagulable by electrolytes. On the other hand, upon evaporating at 40° to 50°, a crystalline, difficultly soluble monohydrate ($MoO_3 . H_2O$), separates out.

The solutions of *telluric acid* and its salts,[4] as also those of *antimonic acid* [5] and its salts, likewise appear, as solutions of semi-colloids, to approach in character the solutions just discussed.

As another limiting case, sols which are almost hydrophobic may be obtained, as prepared by A. Müller [6] in the case of tungstic acid by diluting a solution of tungstic oxychloride $WOCl_4$ in ether-alcohol with water.

The large number of polymerides which are possible in the case of molybdic and tungstic acids renders it probable that the statements of the various workers are in themselves quite correct, although at first they appear to contradict one another; they have simply not succeeded in making the experimental conditions completely comparable. Either the salts from which they start may belong to various polymeric acids, or the conditions for polymerization during the preparation of the sol may be different.

To this group of colloidal solutions also belong those of *molybdenum* and *tungsten blue* [7] which are obtained by reduction of the acids under suitable conditions; molybdenum blue, for instance, by acidifying a solution of ammonium molybdate with H_2SO_4 and reducing with H_2S.

Colloidally dissolved tungstic acid, freshly separated from the solution of the sodium salt by HCl, has, according to Frl. Wassiljewa's experiments,[8] the curious property of being sensitive to light; it is reduced in light by reducing agents such as glucose, formaldehyde, etc., to a blue tungsten

[1] *Sabanajeff*, Journ. d. russ. physik.-chem. Ges. **27,** 53 (1895); **29,** 243 (1897); Abstract: Kolloidzeitschr. **3,** 236 (1908); *L. Wöhler* and *Engels*, Kolloidchem. Beihefte **1,** 454 (1910); *Lottermoser, loc. cit.* p. 508.

[2] *Rosenheim* and *Bertheim*, Zeitschr. f. anorg. Chemie, **34,** 427 (1903); *Rosenheim* and *J. Davidsohn*, *ibid.* **37,** 314 (1903).

[3] It is e.g. present in a decided degree with aqueous solutions of mono-sodium urate [*Schade* and *Boden*, Zeitschr. f. physiol. Chem. **83,** 347 (1913); *Bechhold* and *Ziegler*, Biochem. Zeitschr. **20,** 205 (1909); **64,** 479 (1914)].

[4] *Rosenheim* and *Jander*, Kolloidzeitschr. **22,** 23 (1918).

[5] *Jander*, Kolloidzeitschr. **23,** 122 (1918).

[6] *van Bemmelen*-Festschrift, 1910, p. 416; Kolloidzeitschr. **8,** 93 (1911).

[7] *W. Biltz*, Ber. d. deutsch. chem. Ges. **37,** 1095, 1766 (1904); **38,** 2963 (1905); *Dumanski*, Kolloidzeitschr. **7,** 20 (1910).

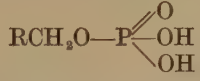
[8] Zeitschr. f. wiss. Phot. **12,** 1 (1913).

compound. In course of time the tungstic acid loses this property. It changes, according to a reaction of the first order, into a form insensitive to light. By warming, the light-sensitive form may again be produced. The two forms also differ in that the light-sensitive one absorbs in the ultra-violet. Whether this transformation is a matter of hydration has not yet been decided; it might be settled by testing whether it is influenced by electrolytes, and, if so, whether this influence has a lyotropic character.

The Hydrosols of Carbohydrates

To this group of sols belong solutions of starch, cellulose, agar, dextrins, and others. As in the case of protein sols, their behaviour is largely ruled by a lively chemical reactivity, so that it is often difficult to decide how far we are dealing with a purely chemical process or with one which is more colloido-chemical in nature.

Colloidal solutions of *starch* are prepared from the natural starch grains occurring in many parts of plants. The structure of these grains will be dealt with in more detail later (p. 725). Here we will only remark that they are gels, which radiographic investigation has shown to have largely crystalline properties. On the other hand, they can imbibe water; that is, the micellæ are separated by films of water, and in these films of liquid or adsorbed on the micellæ are foreign substances, which investigation has shown to be important for the properties of starch sols. This is especially true of the ash (about 0·2 per cent.) held very firmly by the starch grains, which is probably chemically combined with the polyose of the starch micellæ (or with another polyose). The ash consists mainly of phosphates; it is therefore assumed that the phosphoric acid combines with the polyose to a phosphoric acid ester, for instance according to the formula



This constituent of starch containing phosphorus is usually described as *amylopectin*. The micellæ themselves consist chiefly of a phosphorus-free polyose, called amylose.[1]

Amylopectin appears to be chiefly responsible for the behaviour of starch sols. This behaviour may be described somewhat as follows. Starch grains cannot be peptized in the cold in pure water; at about 60° they become pasty, that is, they lose shape and structure by swelling up more strongly and sticking together. By heating starch paste with water in an autoclave at about 120° a sol is obtained. This is, when freshly prepared, very viscous. Its viscosity is greatly altered by acid or alkali, being lowered by acids, and generally raised by alkalis; the conductivity is slight. The sol ages in a very pronounced manner; its viscosity thereby diminishes to such an extent as to be finally little different from that of pure water. It becomes increasingly less alterable under the influence of acids and bases, the conductivity rises. At the same time the originally fairly cloudy sol deposits a small part of the starch in flakes. Hence a

[1] The following description is chiefly in connexion with the work of *Samec*:—Kolloidchem. Beihefte **3**, 123 (1911); **4**, 132 (1912); *Samec* and *v. Hoefft*, *ibid.* **5**, 141 (1913); *Samec*, *ibid.* **6**, 23 (1914); *Samec* and *Jencic*, *ibid.* **7**, 137 (1915); *Samec*, *ibid.* **8**, 33 (1916); **10**, 289 (1919); see further *Bottazzi* and *Victorow*, Rend R. Accad. d. Linc. (5), **19**, II, 7 (1910). [See also *Stocks*, "Starch, gums, hemicelluloses, albumin, casein, gluten, and gelatine," I. B.A. Rep. on Coll. Chem., p. 46.]

clear, slightly viscous sol finally remains, the osmotic pressure of which is not, however, considerably greater than that of the original sol, a sign that ageing does not depend alone upon the production of micellæ of smaller molecular weight from larger ones. It does, however, appear to depend upon the gradual saponification of the amylopectin. This is, as colloidal electrolyte, strongly hydrated, and hence causes, in accordance with a very general assumption (cf. p. 543) the high viscosity originally present. As protective colloid it also peptizes the comparatively large amylose micellæ, which contain less water. The influence of acids and bases perhaps depends partly upon the dissociation of the amylopectin being depressed by acids, the number of its ions and hence the viscosity being reduced, while alkali, conversely, increases both the number of ions and the viscosity. Upon ageing, the amylopectin disappears, since it is saponified, and this causes the reduction in viscosity, the increase in conductivity, and the deposition of the particles which are no longer sufficiently protected.

In favour of this view we have the fact, demonstrated by Samec,[1] that this slightly viscous sol, insensitive to acids and alkali as regards viscosity, is likewise obtained by decomposing or removing amylopectin at the outset by other means. This is accomplished most effectively by the freezing method of Malfitano and Frl. Moschkoff.[2] The natural starch sol obtained in the manner just described is frozen; after thawing the liquid is filtered off and the precipitate peptized anew to a starch sol by heating in the same manner as before; this is then again frozen, and the treatment repeated several times. The substance filtered off thereby sensibly alters in its properties; originally jelly-like, it finally becomes fibrous, paper-like. The sol prepared from the coagulum finally obtained is as little viscous as a greatly aged natural sol, has the same insensitivity towards acids and alkali, and does not change its viscosity in the course of months. A time-change does, however, take place in so far as a certain quantity of starch is gradually thrown down, mostly in fine-grained form.

When the starch grains were freed from ash by Wolff and Fernbach's[3] method by shaking them with dilute (about 0·03 N) HCl, and then washed perfectly free from acid before peptization, sols were obtained which stood, as regards their properties, between those from untreated starch and those of Malfitano and Frl. Moschkoff. This corresponds to the fact that the removal of ash by the Wolff-Fernbach method is not so thorough as by that of Malfitano and Moschkoff.

From this it is readily seen that long-continued heating acts exactly as do alkalis or removal of ash, for at higher temperatures the saponification of the amylopectin is accelerated, especially in the presence of $H^{\cdot}$ ions. Indeed, it appears that in Malfitano's method it is just the repeated heating that is the essential feature of the preparation of the sols. The freezing-out only effects the separation of the electrolyte from the starch. Accordingly, this method is particularly effective when a starch is used treated with acids according to Wolff and Fernbach; acid, of course, strongly favours the saponification of amylopectin.

In accordance with its chemical nature, amylopectin is more decidedly charged than amylose, the charge being negative. Hence fresh starch sols containing amylopectin exhibit a considerable kataphoretic migration velocity; this decreases greatly under the conditions under which amylo-

[1] *Samec* and *v. Hoefft, loc. cit.* p. 635.
[2] *loc. cit.* p. 582.
[3] Compt. rend. **140,** 1403 (1905).

pectin disappears, and attains very small values in greatly aged or ash-free sols.[1]

Further, Samec [2] succeeded in separating amylopectin and amylose, by Mme. Gatin-Gružewska's method,[3] that is, in separating a starch colloid containing phosphoric acid from one phosphorus-free. Starch grains can be peptized by aqueous potash; if a suitable concentration of alkali is chosen (0·12 N. KOH) and with great dilution of the starch sol, a colloid is flocculated upon acidification with dilute H_2SO_4, which contains practically all the phosphoric acid of the original starch. After purifying and drying, it is transparent, gum-like, and migrates decidedly towards the positive pole, is therefore like amylopectin. From the liquid, on the other hand, a colloid is obtained which is almost completely free from phosphoric acid, is a pure white powder when dry, and when peptized shows practically no kataphoretic migration; but the gradual separation of starch flocculi occurs as in the ageing of amylopectin-free amylose sols. Even though we may doubt whether so violent an attack as that produced by alkali gives the same substances as were originally present in the starch grains, we nevertheless evidently obtain two substances which have throughout the properties which we should ascribe to the general behaviour of amylopectin and amylose.

The OH' ion is not the only substance which peptizes starch in the cold. Of other electrolytes, thiocyanates, potassium iodide, and zinc chloride may be named, and of non-electrolytes chloral hydrate in particular. Only the action of dilute solutions of alkali has been investigated in detail by Samec [4]; salt-like compounds, both of amylopectin and amylose, were formed, and the hydration altered greatly in agreement with the general experience that salt-formation is accompanied by a great change in the state of hydration.

Starch sols are very insensitive towards electrolytes, evidently because their peptization is hardly affected by electrical circumstances, but depends essentially upon hydration equilibria, as in the case of a true solution. Electrolytes influence the separation of starch flocculi during ageing, doubtless in the sense of the lyotropic series.

The mean molecular weight of starch in its sols amounts, according to osmotic pressure measurements,[5] to about 100,000. They are accordingly irresolvable in the ultramicroscope. The effect of the operations of dissolving and freeing from ash is to produce a certain, but unimportant, diminution in molecular weight.

This degradation of the starch molecule manifests itself more strongly in the molecular weight of the so-called soluble starches, in which case values of 50,000 and less are probable.[6] They are formed by interaction with various substances: concentrated HCl in the warm, glycerine, potassium permanganate, and others, and deep-seated chemical changes take place in the process.[7]

In the degradation of starch by diastase Biltz [8] attempted for the first time to follow systematically the change in molecular weight, during decom-

[1] *Samec* and *v. Hoefft*, Kolloidchem. Beihefte **5**, 192 *et seq.* (1913).
[2] Kolloidchem. Beihefte **6**, 23 (1914).
[3] Journ. d. physiol. et d. pathol. gén. **14**, 7 (1912).
[4] Kolloidchem. Beihefte **8**, 33 (1916).
[5] *Samec, loc. cit.* p. 559.
[6] *Samec* and *Jencic, loc. cit.* p. 635.
[7] *Samec* and *Jencic, loc. cit.* p. 635.
[8] Ber. d. deutsch. chem. Ges. **46**, 1532 (1913).

position, of a substance of high-molecular weight. He determined a short intervals the viscosity of the starch paste decomposing under th influence of the enzyme, and estimated the mean molecular weight of th substance in solution upon the basis of the fact mentioned on p. 543, tha with the dextrins a regular connexion between viscosity and molecula weight appears to exist. The result was obtained that the diminution i molecular weight takes place initially exceedingly rapidly, and become increasingly more slow, the further the dextrins are degraded.

This result probably has general significance. The first decompositio of large molecules possibly always takes place very quickly, and this i one of the causes why biologically important substances, such as enzymes agglutinins, and so on, are so difficult to obtain and to manipulate wit certainty.

The *dextrin* sols belong—as already pointed out—decidedly to the semi-colloids, which form the transition to true solutions. They diffuse wit fair rapidity, dialyse through ordinary membranes such as collodion an parchment (not copper ferrocyanide), and are quite insensitive towards electrolytes. As properties which their solutions still possess in common with hydrophilic sols, may be named: high viscosity, protective actio towards gold sols, separation in non-crystalline form.

That the taking-up of iodine by starch with formation of blue "iodid of starch" has largely the character of an adsorption, and that many other substances are also able to take up iodine in a similar fashion wit the formation of a blue or violet coloration, has already been discussed earlier (cf. p. 189). Nothing final can be said as to the form in which th iodine is bound. Harrison [1] regards it as probable that the iodine is present in a colloidally disperse form, and that starch as a protective colloid favours this dispersion. It is true that the fact that the blue coloration is adversely affected by substances which dissolve iodine, such as alkalis or organic liquids like chloroform, chloral hydrate and so on, is scarcely conclusive, for the adsorption of any substance in any form in solvents in which it is freely soluble is always small (see p. 195). The fact that iodine in iodine-starch compounds can show very varied colours, from blue through blue-violet to red, without the starch having suffered any detectable chemical change, is more conclusive; but the conditions were so chosen, that the iodine could appear in various degrees of dispersity, and this variation might cause the differences in colour.

Cellulose cannot be peptized in pure water, but successfully so in electrolyte solutions, and when the cellulose has been suitably transformed into other compounds. Among electrolyte solutions are those of $ZnCl_2$, $Ca(CNS)_2$, $CaBr_2$, $LiNO_3$ [2] and similar electrolytes such as are also effective with starch, and then particularly the alkaline solution of copper oxide in ammonia, the so-called Schweizer's reagent.[3] The micellæ of these sols certainly do not consist of unchanged cellulose, but of more or less degraded and hydrated derivatives; this follows from the fact alone that when cellulose is precipitated from these sols, for instance, by acidifying the cellulose solution prepared with Schweizer's reagent, the separated substance

[1] *loc. cit.* p. 189.

[2] *v. Weimarn*, Kolloidzeitschr. **11,** 41 (1912); *R. O. Herzog* and *F. Beck*, Zeitschr. f. physiol. Chemie, **111,** 287 (1920).

[3] *Schweizer*, Journ. f. prakt. Chemie, **76,** 109, 344 (1857). On the behaviour of these cellulose sols on dialysis see *Grimaux*, Compt. rend. **98,** 1434 (1884).

has properties differing from those of the original cellulose. It is, for example, usually more sensitive to water, that is to say, has a stronger tendency to imbibition and loses strength thereby.

The so-called viscose solutions,[1] which are so important in the artificial textile industry, are cellulose sols of a somewhat different kind.[2] If a mercerized cellulose, that is, one treated with and containing alkali, be moistened with carbon disulphide, it liquefies fairly quickly into a slimy brownish yellow mass, which contains cellulose xanthogenate, and is easily peptized to sols by shaking with water; the liquids are strongly alkaline. Upon acidification substances are thrown down which are closely related to the original cellulose, though they are generally more sensitive to water.

The kind of cellulose, whether cotton, wood-fibre, and so on, and the previous treatment (mercerization, etc.) influence the peptization and the properties of the resulting sol. All these colloidal solutions show great changes with time; these are due to chemical changes (hydration, etc.). With many, ageing reminds one of starch sols inasmuch as the originally viscous sols tend towards an increasingly less viscous state. On the other hand, others, such for instance as viscose solutions, become increasingly more viscous in course of time, until they set to jellies. The whole behaviour of cellulose sols renders it probable that, like the starch sols, they contain micellæ of different kinds; on the one hand those consisting of cellulose comparatively little altered, and on the other of more extensive degradation products, which act as protective colloids and, being particularly strongly hydrated, cause the high viscosity.

As already remarked, these sols play an important part in the technical production of artificial fibres. The method consists in pressing the sol through a fine orifice into a liquid, in which the viscous stream of liquid coagulates to a solid thread. Dilute sulphuric acid is used as coagulating solution in the case both of cuprammonium cellulose sols and of viscose solutions. It is important that the sol should be of the right strength and also have suitable properties in other respects, and this is attained by a proper preliminary treatment of the cellulose and correct ageing. As far as is known, practical experience is the only guide. It is not known from theoretical considerations what chemical and colloido-chemical properties of the micellæ are of importance.

Perhaps it is important that the following conditions are fulfilled. The little altered cellulose micellæ of the sols should not be spherical, but must rather be rod-shaped or at least parallelopipedal, so that they lie well together as the thread is pressed out. They are certainly not so elongated as those of the V_2O_5 sol (cf. p. 404), for they do not give the phenomena there described; it is true that the phenomena, if present, would be less marked by reason of the smaller difference in refractive index between micellæ and intermicellar liquid. The more changed and further degraded micellæ no doubt act in coagulation as cement between the micellæ forming the structure.

The colloidal solutions of *agar* also belong to these carbohydrate sols.

[1] *Cross, Bevan* and *Beadle*, Ber. d. deutsch. chem. Ges. **25**, 1090, 2524 (1893); **33**, 1513 (1901).

[2] As comprehensive descriptions of this subject may be named: *F. Becker*, "Die Kunstseide," Halle, 1912. *Süvern*, "Die Künstliche Seide," 3rd ed., Berlin, 1921. [See also *Harrison*, II. B.A. Rep. on Coll. Chem., article "Colloid Chemistry in the Textile Industries," which contains a large number of references.]

Agar, a mucilage which is obtained in China from seaweed, contains beside proteins and other constituents, particularly a polyose, called gelose. According to recent investigations of de Jong [1] one can plainly recognize with agar sols how the stability is determined both by electrical influences and by hydration; it has thus a pronounced likeness to the Odén sulphur sol. The sols of agar are distinguished by the fact that they set to jellies at a very low agar content (cf. details, p. 706).

The Hydrosols of the Proteins

The protein sols [2] have already been considered in detail in the General Part. In connexion with them a number of typical phenomena were discussed: the isoelectric point due to their amphoteric nature, the peptizability by small concentrations of electrolytes, the salting-out by larger concentrations, the transition from a hydrophilic behaviour to a hydrophobic on account of denaturing, etc. It was also repeatedly emphasized that on account of their great chemical reactivity they tend to interact chemically with many substances, so that the necessarily ill-defined boundary between the purely chemical and the colloido-chemical are in their case particularly difficult to determine.

Some further examples of this may be discussed. Heavy metal salts, such as $ZnSO_4$, $CuCl_2$, etc., even in small concentrations, generally precipitate protein sols. If we take the chemical standpoint we shall suppose that a difficultly soluble heavy metal salt of the protein acting as acid is formed, or a salt containing a heavy metal protein complex. But this precipitation differs from the ordinary precipitation of a difficultly soluble salt, in so far as the precipitate is frequently soluble in excess either of the protein sol or of the heavy metal salt. A pronounced irregular series can be observed: lower non-flocculation zone, lower flocculation zone, upper non-flocculation zone, upper flocculation zone (cf. p. 429). One would prefer after all to regard this as peptization and reversal of charge, unless one is prepared to reckon with a whole series of complexes of different properties. We are also reminded of colloido-chemical processes by the fact that the flocculation of protein sols by salts of heavy metals is sensitive to electrolytes; if we work with a sol as free as possible from electrolytes, flocculation is slight or absent.[3] This behaviour recalls the sensitization of Fe_2O_3 sols by proteins (cf. p. 583). Perhaps we shall be compelled to distinguish between the loose and at first usually reversible adsorption compound of protein and heavy metal salt (or heavy metal hydroxide) and the actual heavy metal salts formed in course of time, just as in the case of the interaction of aluminium hydroxide and Congo blue (cf. p. 236).

The same difficulties are met with in explaining the actions of dye solu-

[1] "Het Agarsol." Diss., Utrecht, 1921.

[2] As comprehensive descriptions of the chemistry and colloid chemistry of the proteins may be mentioned: *Cohnheim*, "Chemie der Eiweisskörper," Brunswick, 1911; *Plimmer*, "The Chemical Constitution of the Proteins," 2nd Ed.; *R. O. Herzog*, "Eiweisskörper" in vol. IV, p. 494, of the Enzyklopaedie der technischen Chemie, Berlin, 1916; *Pauli*, "Kolloidchemie der Eiweisskörper," 1st half, Dresden and Leipzig, 1920. [See also *Matthews*, "Physiological Chemistry," 1916; *McClendon*, "Physical Chemistry of Vital Phenomena," Princeton Univ. Press, 1917; *Mann*, "Chemistry of Proteids," Lond., 1906 (based on Cohnheim); *Brailsford Robertson*, "Physical Chemistry of Proteins," Lond., 1918; *Plimmer*, "Chemical Constitution of Proteins," 2 vols., Lond. (1912–1913); *Osborne*, "Vegetable Proteins" (Longman's monographs)].

[3] See *Pauli, loc. cit.*, p. 589.

tions upon protein sols.[1] Here also is the behaviour simple only in a few cases, and such as would correspond to the precipitation of a difficultly soluble salt : complete precipitation, as soon as a certain dye concentration is reached, which remains thus unchanged even with larger dye and protein concentrations. This is the case, for instance, in the action of methylene blue upon hæmoglobin and upon both natural and denatured serum albumin.[2] With most other dye solutions we again encounter irregular series, and usually of a kind in which a flocculation zone lies between two non-flocculation zones, without an upper flocculation zone. That this is missing may naturally have its cause in the attainable high concentrations of the dye solution being insufficient for the one dye ion to flocculate the protein sol with its charge reversed in sign by the other dye ion. The behaviour thus recalls the interaction of two hydrophobic sols (cf. p. 477), and suggests a peptization caused by reversal of charge. It appears to be largely true that under conditions under which protein kations are formed, that is to say, in acid solution, acid dyes flocculate ; conversely basic dyes flocculate, when protein anions are formed, that is in alkaline solution.

The precipitation of protein sols by acids, such as phosphomolybdic, silicotungstic, phosphotungstic, hydrochloroplatinic, hydrochloroauric, and others, which contain complex ions, appears to correspond to the precipitation of a difficultly soluble salt without further complications. Here again one works in acid solution ; hence protein kations are present in considerable amount.

The proteins are known to be built up from polypeptides. By peptides are understood chains of amino-acids, which are linked together by the group — CO — NH —. The simplest peptide, for instance, is glycyl-glycine

$$NH_2 — CH_2 — CO — NH — CH_2 — COOH.$$

Emil Fischer and his co-workers built up a large series of polypeptides, including some with high molecular weights, as for instance the octadeca-peptide leucyl-triglycyl-leucyl-triglycyl-leucyl-octoglycyl-glycine with the molecular weight 1213.[3] As to how the colloido-chemical properties alter as we pass from a peptide of low to one of high molecular weight, little is known at present. An important advance in this direction is the work of Abderhalden and Foder [4] on the adsorption of peptides and aminoacids by charcoal. Up to the present substances of small molecular weight, which therefore give true solutions, have been chiefly investigated ; but their behaviour should be important in so many respects for protein solutions, that a discussion of them is in place here.

For substances such as *d*-alanine (*α*-aminopropionic acid), *l*-leucine (*α*-aminoisocaproic acid), *d*-alanyl-*l*-leucine, *l*-leucyl-glycine, glycyl-*l*-leucine the commonly observed rules of adsorption largely hold, e.g. in moderate concentrations the ordinary adsorption isothermal, the exponent of which is 1 for small concentrations (cf. p. 234). Like the hydroxy-acids, they are substances which are only slightly adsorbed at the water-air

[1] See *Heidenhain*, Pflüg. Archiv, **90**, 115 (1902) ; **96**, 440 (1903) ; **100**, 217 (1903) ; *L. Michaelis*, *ibid.* **97**, 606 (1903).

[2] These and the following statements depend upon experiments by *Buxton* and *Teague*, Zeitschr. f. physik. Chem. **62**, 287 (1918).

[3] *E. Fischer*, Ber. d. deutsch. chem. Ges. **40**, 1754 (1907).

[4] Fermentforschung, **2**, 74 (1917) ; **2**, 151, 217 (1918) ; Kolloidzeitschr. **27**, 49 (1920).

surface, which therefore influence the surface tension but little, while their adsorption on charcoal is appreciable. It follows from this that it depends on the affinity between adsorbent and adsorbed substance, and not only upon larger differences in the affinity towards water molecules. In agreement with this, the adsorption is fairly specific; glycine is scarcely adsorbed at all, alanine is distinctly adsorbed, leucine, and especially compounds of higher-molecular weight, such as *d*-alanyl-*l*-leucine, more strongly. But even these do not belong to the strongly adsorbable substances; of *d*-alanyl-*l*-leucine in 0·01 molar solution, 0·14 millimol per gram is adsorbed by charcoal (cf. p. 198, Table 69). A relation to the solubility is not pronounced, in accordance with a predominance of the affinity to the adsorbent; the more soluble *l*-leucyl-glycine is more strongly adsorbed than the less soluble glycyl-*l*-leucine.

In the adsorption of these substances from mixtures with other substances peculiar divergences from the normal behaviour are in fact found. If the added substance is not a peptide or amino-acid, but a sugar, or a nearly related substance not containing an amino-group, such as glycine anhydride or pyrrolidone-carboxylic acid, the adsorption of the mixture follows throughout the ordinary rules (cf. p. 199); both substances are more weakly adsorbed from the mixture; they mutually displace one another. If, on the other hand, we have a mixture of amino-acids or polypeptides, we meet with the following behaviour. The substance more weakly adsorbable from pure solution is displaced; the more strongly adsorbable one, on the other hand, is more strongly adsorbed from the mixture than from pure solution; so much more strongly, that the adsorption, calculated on amino-nitrogen, is about as large as if the amounts of each of the pure substances adsorbed from pure solutions of the same concentrations are calculated in the same way and added together. This behaviour is entirely reversible. It is conceivable that after further experiment it will be possible to understand it on the basis of Langmuir's theory (cf. p. 130), if we assume that residual valencies are present on the charcoal which are preferentially saturated by amino-groups.

The aspect which the relationships assume when we pass to peptides of higher molecular weight,[1] and when further the adsorption of peptides or proteins (such as elastin, keratin, and the like) as adsorbents is investigated, and whether phenomena do not then appear which correspond to the specific adsorption of agglutinins, toxins, and the like, all deserve special attention.

The changes which occur in the properties as we proceed from truly dissolved peptides of low molecular weight to colloidally dissolved ones of high molecular weight have scarcely been systematically investigated. As far as experiments go up to the present it may be said that the length of the polypeptide chain produces an effect, but is only one of the influences which determines the behaviour. Thus it favours the hydrolytic decomposition by pancreatic juice,[2] but structural and stereochemical circumstances are of no less importance. That the biuret reaction—the rose or violet coloration under the action of a little copper sulphate and much alkali—becomes increasingly more decided as we pass to higher peptides,[3]

[1] According to *Grimaux* [Compt. rend. **93,** 771 (1881); **98,** 231, 1336 (1884)] the behaviour of his "artificial proteins," that is, mixtures of polypeptides of high molecular weight, is very similar to that of the natural proteins.

[2] *E. Fischer* and *Abderhalden*, Zeitschr. f. physiol. Chemie, **46,** 52 (1905).

[3] *E. Fischer*, Ber. d. deutsch. chem. Ges. **39,** 580 (1906).

is probably only an indirect influence of the length of the chain. According to Schiff [1] this reaction presupposes a certain constitution, namely, two $-CONH_2$ or $-CSNH_2$ or $-C\begin{matrix}NH\\ \diagdown\\ NH_2\end{matrix}$ groups which may only be separated from one another by one C or one N atom, and its appearance is favoured by a long chain. The possibility of various complex copper salts is very great,[2] so that a comparison of this reaction of the proteins with similar reactions of simpler organic substances is not immediately decisive. In the case of precipitation by phosphotungstic acid the size of the molecule is obviously a very decisive factor; it appears with many tripeptides in concentrated solution; from the octapeptides onwards it proceeds exactly as in the case of the proteins.[3] Salting-out, on the other hand, behaves entirely as an effect on the solubility. Accordingly, it does not depend alone on the length of the chain; on the contrary, if the peptides contain amino-acids which are in themselves less soluble in water, such as tyrosine or cystine, they may also be salted out more easily.[4] The coefficient of diffusion, the viscosity, the gold and iron numbers have not yet been tested for a polypeptide series.

Such an investigation should lead to more definite results than an examination in this manner of the degradation products of proteins, the albumoses and peptones. These are probably not single substances, but mixtures of peptides. In their properties in solution they entirely represent the transition to truly dissolved substances and hence stand towards the proteins as do, for example, the dextrins to starch. Thus peptones dialyse through the usual membranes. The conductivity of their solutions is such that conclusions may be drawn as to their basicity, and the dissociation is so strong that they have no protective effect on gold sols, but flocculate them.[5] But on the other hand they are readily transformed, even when they merely spread out upon a water surface, into nearly related substances which are difficultly soluble in water and form tough amorphous solid skins.[6]

Since nothing is yet known concerning this connexion between the constitution of the polypeptides and their colloido-chemical properties, nothing whatever is known concerning the relations between the structure of the various proteins and their colloido-chemical peculiarities. It may only be pointed out that, although the proteins are all amphoteric on account of their chemical structure, the differences in their acidic or basic character are much greater than one would perhaps assume from the differences in the isoelectric point given on p. 574. Some are decidedly acidic, like casein, in which however the amphoteric character is shown by its solubility in concentrated acids; and some decidedly basic, such as the histones and protamines, which in consequence of this property are at first precipitated by alkalis, and only become soluble again in more concentrated solutions of alkali. The protamines are such strong alkalis that one

[1] Lieb. Ann. **299,** 236 (1898).
[2] *Ley* and *F. Werner,* Ber. d. deutsch. chem. Ges. **46,** 4040 (1913).
[3] See *R. O. Herzog,* "Die Eiweisskörper," p. 499.
[4] *R. O. Herzog,* "Die Eiweisskörper," p. 503.
[5] See *W. Neumann,* Zeitschr. f. physiol. Chemie, **45,** 216 (1905); *Siegfried, ibid.* **45,** 252 (1905).
[6] See *Metcalf, loc. cit.* p. 535.

chiefly only meets with their salts. Clupein sulphate, mentioned in Table 143, p. 547, is an example of such a protamine salt.

In the case of naturally occurring protein solutions we are dealing almost throughout with mixtures of proteins of different kinds. In order to separate them the property is usually taken advantage of that they are preferentially salted out by different electrolytes at different concentrations of the latter; that is to say, their solubility in these solutions is different. This method was worked out by Hofmeister and his co-workers.[1] For instance, fibrinogen (contained in blood) is difficultly soluble; it is completely precipitated in unsaturated $MgSO_4$ and NaCl solutions and in $\frac{1}{3}$ saturated $(NH_4)_2SO_4$. The limit of precipitation is frequently characterized by the number of cubic centimetres of a saturated $(NH_4)_2SO_4$ solution which must be added to 10 c.c. of the protein solution in order to precipitate it. The upper limit of precipitation for fibrinogen thus lies at about 3. In the case of globulin the protein solutions must be saturated with MgSO and NaCl; for $(NH_4)_2SO_4$ the limit lies between 2·7 and 4·6. At 2·7, the lower limit of precipitation, the globulin begins to separate. The most soluble proteins, albumin and hæmoglobin, are not precipitated by MgSO and NaCl even in saturated solution, by $(NH_4)_2SO_4$ only at saturation. In order to free the proteins from electrolytes, the electrosmotic purification described on p. 378 is to be recommended, in which it must be noted that in order to avoid disturbances, the sulphates are best replaced by other electrolytes, such as acetates.[2]

The globulins which are precipitated within the precipitation zone mentioned may be divided into two groups: the *euglobulins*, which are only soluble in dilute solutions of electrolyte, and the *paraglobulins*, which dissolve in pure water (cf. pp. 587 and 593).

An extensive separation of globulins and albumins can therefore be effected by removal of the electrolytes by dialysis. Hence if a blood serum be dialysed, euglobulins soon separate freely on the membrane, and the supernatant colloidal solution contains almost entirely only albumins and paraglobulins.

Also in the rate of denaturing and in the temperature coefficient of this rate considerable differences have been found. Upon these depend the different coagulation temperatures of proteins; their value as a means of characterization is limited by the sensitiveness to other influences mentioned above (p. 613). Regarding the denaturing at various interfaces, such as clay and charcoal, the proteins also differ noticeably. Thus calcium caseinate, fibrinogen and others are denatured by animal charcoal and burnt clay. Hence they cannot be filtered through earthenware cells, while sodium caseinate, albumin, and others pass through unhindered and are not denatured.[3] On iron oxide, albumin is partially denatured, as appears from the incompletely reversible adsorption (cf. p. 536).

Soap Solutions and Saponins

The essential features of *soap* solutions, which are remarkable in a high degree as colloid electrolytes, have already been dealt with earlier. Here we shall deal especially with the further question: at what length of the

[1] A summary of this work is given in *Cohnheim*, "Chemie der Eiweisskörper," p. 160 [*Mann*, "Chemistry of Proteids," Lond., 1906].

[2] F.P. 518,119; cited from Chem. Zentralbl. 1921, II, 330.

[3] *Hermann*, Pflüg. Archiv, **26**, 442 (1881); further also *Zahn*, *ibid.* **2**, 598 (1872) *J. Lehmann*, *ibid.* **56**, 558 (1894).

carbon chain, as we ascend the homologous series, does the soap-like character of the fatty acid salts appear? It has already been mentioned above (p. 567) that a divergence in osmotic behaviour as compared with that of potassium acetate is noticed at about potassium octoate, while the peculiarities which distinguish soap solutions as regards their conductivity appear at about potassium laurate. Here only the capillary-active behaviour of soap solutions will be considered, since in this respect they are particularly remarkable. Donnan[1] made experiments as described above on p. 601. He determined the number of drops with which a certain volume of a hydrocarbon containing fatty acid distributed itself in a millimolar NaOH solution; while this drop-number was about 37 with the lower fatty acids, it rose with octoic acid (C_8) to 47, with lauric acid (C_{12}) to 82. Experiments by Donnan and Potts[2] led to the same result, that a decided surface activity first appears at sodium octoate. They measured the interfacial tension of a solution of the sodium salt of a fatty acid in various concentrations against a pure hydrocarbon. With the salts of the lower fatty acids up to heptoic acid the interfacial tension was lowered comparatively little, in proportion to the concentration of the salt. Almost suddenly a strong depression of the interfacial tension appeared at sodium octoate; the σ, c curve had the strongly curved form which distinguishes the capillary-active substances (cf. p. 61). In Fig. 123 the number of carbon atoms in the fatty acid salts are plotted against the relative values of the interfacial tension as observed in 2·5 millimolar solution; the first drop at octoic acid (C_8), and the still sharper one at decoic acid (C_{10}), are recognizable.[3]

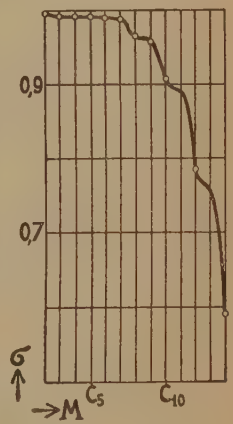


Fig. 123.—Decrease of Interfacial Tension with Rise in the Homologous Series of the Sodium Salts of the Fatty Acids.

The workers in question now proceeded to test the power of the sodium salt to emulsify the hydrocarbon, by producing an emulsion of the hydrocarbon with the salt solution by energetic shaking and determining after a certain time of settlement the oil content of the aqueous phase. It appeared that sodium laurate and myristate were the first to have a definite emulsifying power; sodium nonoate and octoate had none. This is apparently in contradiction to the capillary-active behaviour. It is however explained by the following result. The emulsifying power has, in the case of the laurate and myristate, a sharply defined maximum. With sodium myristate, for example, in a concentration of 3·3 millimolar about 15 per

[1] *loc. cit.* p. 601.

[2] Kolloidzeitschr. **7**, 208 (1910).

A. Mayer, Schaeffer, and *Terroine,* Compt. rend. **146,** 484 (1908) wish to put the first appearance of colloidal properties at hexoic acid (C_6) chiefly on the ground of ultramicroscopic results.

[3] It appears questionable whether the curve drawn by *Donnan* and *Potts,* in which the points are connected by straight lines, is correct, or whether, in accordance with the course given in Fig. 123, undecoic acid only lowers the interfacial tension a little more than decoic, and tridecoic a little more than lauric, just as nonoic is found to lower it only a little more than octoic. No doubt here again the periodic change in many properties in ascending the homologous series makes itself felt [see e.g. *Biach,* Zeitschr. f. physik. Chem. **50,** 43 (1905)].

cent. of oil was emulsified, at 1·67 and 5 millimolar only 1 per cent. and 6·5 per cent. respectively. The cause of this behaviour is unquestionably the flocculating action of the sodium ion, which makes itself felt upon the negative droplets at higher salt concentrations. It may be reasonably supposed that the weak emulsive power which is to be expected with octoate is masked by the coagulating influence of the kation. It may be remarked that Spring [1] in bringing soot into suspension by means of soaps observed a pronounced maximum in the suspending power.

As opposed to the soaps, the *Saponins* have been comparatively little investigated from the colloido-chemical point of view. They are glucosides, which contain besides the sugar residues the sapogenins, the constitution of which has not yet been elucidated in detail. In them, at any rate, aromatic and terpene-like complexes are to be assumed.[2] From known data we can deduce that the saponins, in contrast to the soaps, behave in aqueous solution far more as non-electrolytes or as weak electrolytes; many of them, such as quillaja acid, polygala acid, are described by Kobert [3] as weak acids. The solution of a saponin supplied by Merck had, according to Spring,[4] only a slight conductivity. The saponin micellæ proved negative upon kataphoresis. This should be generally true in view of the weak acidic nature of these substances. Like the soaps, the saponins are exceedingly capillary-active. This follows in the first place from the fact that they strongly depress the surface tension of water, and give solid surface films in a high degree (cf. p. 749). Here again this not only depends upon pure adsorption, but also upon a further chemical change, for the films cannot be readily repeptized by water. It is a consequence of the formation of films and lowering of the surface tension that the saponin solutions, even when very dilute, froth strongly. Upon this depends their technical application in the preparation of foaming drinks. Their capillary activity and hence their adsorbability also make themselves evident at the interface solid—liquid. Thus they emulsify oils,[5] and protect soot suspensions,[6] and their solutions may be used for washing. The powerful physiological effects of the saponins are probably also, in part, connected with their strong adsorbability; thus an adsorption upon the gills of fish appears to determine the striking poisonous effect of the saponins upon these creatures.[7] On account of the strong depression of the surface tension and the interfacial tension they render difficultly wettable substances more easily wetted. One is tempted to bring this strong capillary activity of the saponins into connexion with the fact that the sapogenins contain aromatic complexes.

Like the soaps, the saponins give solutions which form the transition to true solutions. For they dialyse, although slowly, through membranes. Electrolytes appear to salt them out only at large concentrations, as is evident from experiments by Kobert [8] with $(NH_4)_2SO_4$. Nevertheless, the micellæ are large enough to have decided adsorptive power, particularly

[1] Bull. d. l. Soc. chim. d. Belg. **24**, 17 (1910).
[2] See e.g. *Winterstein* and *Maxim*, Helv. chim. act. **2**, 195 (1919).
[3] "Beiträge zur Kenntnis der Saponin-substanzen," Stuttgart, 1904.
[4] Bull. d. l. Soc. chim. Belg. **24**, 446 (1910).
[5] *Kobert*, p. 3 of monograph, *loc. cit.*
[6] *Spring*, *loc. cit.* under [4].
[7] *Kobert*, pp. 76–77 of monograph, *loc. cit.*
[8] P. 20 *et seq.* of monograph, *loc. cit.*

for dyes, and apparently in accordance with their negative charge, preferentially for basic dyes. Kobert [1] proved this in two ways. From a saponin solution to which methylene blue had been added the saponin was precipitated by $(NH_4)_2SO_4$ deeply coloured. If a saponin solution is dialysed against a methylene blue solution, the dye collects in the sol to such an extent that its concentration there exceeds that in the outer solution.

Altogether we may say that the saponins give, like the soaps, strongly capillary-active semi-colloidal solutions, but as opposed to the latter are to be regarded rather as non-electrolytes.

Hydrosols of Lecithin and Allied Substances

The lecithins (and doubtless also allied substances such as the cephalins [2]) give aqueous colloidal solutions when dissolved in liquids such as ethyl ether, the solution poured into an excess of water, and the ether removed by a current of air. In their method of preparation, therefore, they resemble hydrophobic sols, and they are closely related to them in properties, but they differ from them in various respects, so that they may, like the not dissimilar Odén sulphur sols, be classed among the hydrophilic sols.

Like these, they are, according to the experiments of W. Koch,[3] Porges and Neubauer,[4] and Long and Gephart,[5] very insensitive towards the salts of the alkali metals ; many, such as NaBr, KI, NaI, did not flocculate them at all under Porges and Neubauer's conditions ; others, such as $NaNO_3$ and KCl, very weakly. The lyotropic series has the reverse order of that with the Odén sulphur sol ; LiCl coagulated strongly in medium concentrations, NaCl weakly, KCl still more weakly. It is frequently observed, e.g. with LiCl and NaCl, that repeptization occurs (as in the case of the Fe_2O_3-albumin sols and others : cf. p. 586) at higher salt concentrations. Bivalent kations coagulate in far smaller concentration ; with many two flocculation zones and repeptization at the highest concentrations were found, and similarly complicated relations appear with tervalent kations and heavy metals. Alkalis peptized markedly.

All this indicates that, although the negative charge of the lecithin has a certain importance, the influence of hydration strongly preponderates. In agreement with this we have the fact that in the coagulation by mixtures of electrolytes an ionic antagonism appears, perhaps still more clearly than found in Odén's sulphur sols. Neuschloss [6] was the first to describe it. His method of experiment was somewhat different from that usually employed. He followed the changes in the surface tension of lecithin sols under the influence of electrolytes, a change that is unmistakably connected with the coagulation. Against the drawback that the method is an indirect one may be placed the advantage that possibly finer changes may be recognized than when we come to coarse and externally visible flocculation. The following relation exists between the surface tension of a lecithin sol and its coagulation. The pure lecithin sol has a smaller surface tension

[1] P. 31 *et seq.* of monograph, *loc. cit.*

[2] The hydrosol of humulon (*α*-hop bitter acid) is, according to *Lüers* and *A. Baumann* [Kolloidzeitschr. **26**, 202 (1920)], similar to the lecithin sols as regards coagulation by electrolytes and influence upon the surface tension.

[3] Zeitschr. f. physiol. Chemie, **37**, 181 (1903).

[4] Biochem. Zeitschr. **7**, 152 (1908).

[5] Journ. Amer. Chem. Soc. **30**, 895 (1908).

[6] *loc. cit.* p. 461.

than water at room temperature; about 55 dyne/cm. Upon addition of an electrolyte the surface tension increases with increase of electrolyte concentration, reaches a maximum, and then decreases again. This effect is explained by Neuschloss on the grounds that the lecithin micellæ are first coagulated by the electrolyte. Thus a diminution in the surface activity of the lecithin is caused, since the coarser flocculi act less upon the surface tension than the finer micellæ present in the pure sol. This is confirmed in so far as the maximum of the surface-tension salt-concentration curve is actually reached at a higher concentration for univalent than for bivalent kations, and for the latter at a higher concentration than for tervalent kations. The decrease in surface tension occurring at still higher electrolyte concentrations depends upon the peptization then occurring.

It was possible to find mixtures of electrolytes having a common anion and different kations which produced an excessively small increase in σ, in contrast to the behaviour in solutions of the pure electrolytes, while with other mixtures this increase was not seriously different from that in solutions of the pure salts. If for instance NaCl and $CaCl_2$ stand in the ratio 1 : 1, then we have a maximum of 67 at a total concentration of 0·125. With the ratio 1 NaCl : $\frac{1}{20}$ $CaCl_2$ we have a maximum only just indicated of 56, with a somewhat higher total concentration of 0·25 molar. Now it is, as Handovski [1] points out, not very advantageous to consider with Neuschloss the surface tension in its dependence upon the total concentration of electrolyte. But even when his results are recalculated, taking the surface tension as a function of the concentration of the one electrolyte, while that of the other remains constant, only a slight change in the surface tension is found in the region of greater concentrations with the ratio Na : Ca observed by Neuschloss. For the mixture of Na and K the results of Neuschloss cannot be maintained after this recalculation, although here also the abolition of the tension-raising action of one salt by a second is unmistakable.

If therefore the influence upon the surface tension is interpreted as a coagulation, we obviously have a pronounced kationic antagonism; the flocculation produced by one kation can be abolished by a suitable concentration of a second, and further, a bivalent one is able to do this towards a univalent one, as also such various kations of like valency as $Na^{\cdot}$ and $K^{\cdot}$ ions, or $Mg^{\cdot\cdot}$ and $Ca^{\cdot\cdot}$. Tervalent appear to act more strongly than divalent, in so far as the balance (referred to the total concentration) is found in a mixture of NaCl + $AlCl_3$ at a ratio 1 Na : $\frac{1}{100}$ $AlCl_3$.

Neuschloss attempts to explain this behaviour on the basis of the adsorption of the kations. This is improbable, since according to the results of P. Scholz (cf. p. 460) the antagonism is practically absent with strongly hydrophobic sols, while it becomes stronger when we pass to more hydrophilic ones. I should thus prefer to assume that hydration influences are in the first place responsible for it.

Quite independently of every interpretation we can agree with Neuschloss that these phenomena are similar in nature to the action of mixtures of electrolytes in many biological processes, in which the influence of a kation, such as $Na^{\cdot}$, is abolished by the addition of another, usually a multivalent one. The experiments of Lillie mentioned above (p. 469) on the behaviour of the cilia of the larvæ of *arenicola* belong here; the liquefying action of the $Na^{\cdot}$ ion is removed by bi- or tervalent kations. Some

[1] Pflüg. Archiv, **185**, 7 (1920); further *Neuschloss, ibid.* **187**, 136 (1921).

further cases may be mentioned. Thus the experiment of Ringer,[1] which forms the starting-point for the investigation of all these biological actions of salts, belong here ; when placed in pure NaCl solution muscles enter into contractions, which disappear again on addition of $Ca^{\cdot\cdot}$ ions. Then the experiments of J. Loeb [2] on fertilized eggs of a sea-urchin, *Fundulus Heteroclitus* : in pure NaCl solution they do not develop to embryos, but do so when the poisonous effect of the NaCl is nullified by small concentrations of bivalent kations such as $Ca^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Mn^{\cdot\cdot}$ ions, indeed even $Pb^{\cdot\cdot}$, $UO_2^{\cdot\cdot}$ and others ; small amounts of tervalent kations act in the same way. An abundance of further examples, particularly from the investigations of J. Loeb, Herbst, Lillie, Wo. Ostwald and others are found in Höber's " Physikalischer Chemie der Zellen und Gewebe " (4th edition, p. 521 *et seq.*). The biological effects of electrolytes also resemble those observed in the case of lecithin and Odén sulphur sols, in so far as the multivalent kations which remove the poisonous effect do not simply act equally strongly in equimolecular concentration, as in the coagulation of purely hydrophobic sols, but are unmistakably of different degrees of efficiency. It might be regarded as a contradiction to the biological behaviour of salt mixtures, that an antidotal action of $K^{\cdot}$ ions upon $Na^{\cdot}$ ions is frequently described, but not one of $Na^{\cdot}$ ions upon $K^{\cdot}$ ions, while in the experiments of Neuschloss both the mixture 1 NaCl : $\frac{1}{2}$ KCl and $\frac{1}{2}$ NaCl : 1 KCl showed the most pronounced antagonism. But Neuschloss [3] was able to show that, for instance, in the influence of electrolyte mixtures upon hæmolysis both mixtures of this kind are effective, just as in the coagulation of lecithin sols.

Höber [4] rightly develops the view that the regular course of the life-processes in question depends upon some colloids or other being present in a certain state of coagulation or peptization. If, for instance, a gel is too strongly peptized, it becomes too permeable, while correct coagulation guarantees the right degree of permeability. Too strong coagulation and too strong peptization both act destructively, and the advantageous mixtures of electrolyte are distinguished by the fact that they hold the balance between flocculation and peptization in the correct manner. The presupposition for such action obviously is, that the states of flocculation and peptization respectively shall be set up readily and reversibly. Lecithin and Odén sulphur sols are distinguished by these characteristics, and are similar for the reason that in their case reversible flocculation and peptization take place in the same way ; in order that they may appear, hydration processes are doubtless always requisite. The similarity might go even further ; even in the case of biological phenomena it is perhaps a matter of a comparatively hydrophobic mixture of colloids (corresponding to sulphur) being peptized and made more hydrophilic in its whole behaviour by degradation products or colloid ions (corresponding to the pentathionic acids).

The Solutions of Organic Dyes

In the case of organic dyes, solutions of very different kinds are encountered. We are mostly dealing with electrolyte solutions. But on the one hand there are dyes which differ in no way from solutions of a

[1] Journ. of Physiol. **4**, 29, 222, 370 (1883) ; **7**, 118, 291 (1886) ; **11**, 369 (1890) ; **16**, 1 (1894) ; **18**, 425 (1895), Proc. Physiol. Soc. 1883, p. VI.
[2] Amer. Journ. of Physiol. **6**, 411 (1902) ; Pflüg. Archiv, **88**, 68 (1901).
[3] Pflüg. Archiv, **181**, 40 (1920).
[4] P. 530 of monograph cited in text.

strongly dissociated electrolyte with organic ions, and on the other hand those which can be at once regarded as hydrophobic sols, while others appear to be more like hydrophilic sols.

Many colloidal dye solutions are so markedly hydrophobic that they have already been mentioned earlier (p. 420) as examples of hydrophobic sols. If this account of the dyes is placed amongst the hydrophilic sols, it is because many dye solutions are semi-colloidal, and the properties of such solutions may be much more conveniently considered in connexion with hydrophilic sols. This does not mean that semi-colloids may not have an entirely hydrophobic character. Dye solutions are very frequently solutions of colloidal electrolytes, in which the dye ion represents the micella ion. The micellæ are so small that the conductivity resembles that of ordinary solutions; but they are still large enough to allow the processes of coagulation and the like to occur.

It has been attempted from various sides to investigate and characterize the dye solutions. That the results obtained are not entirely consistent has two main causes. In the first place, dyes are not well defined as chemical individuals, and one does not therefore know whether the different workers were really dealing with the same substance. Further, the methods of investigation differ in value. One will ascribe most weight to free diffusion, and then to the behaviour upon dialysis and ultra-filtration.[1] By way of limitation we must however take into account the circumstance mentioned earlier (p. 647), that, in presence of colloidally dissolved substances, the dialysis of truly dissolved substances may be hindered, if their molecules are strongly adsorbed by the micellæ of the colloid. The ultramicroscopic results will be made use of with still greater caution.[2] Individual micellæ may be due to impurities and need not be characteristic of the dye. On the other hand the field of view may be empty since the micellæ are too small and the refractive indices of micellæ and intermicellar liquid do not differ sufficiently. Of the dyes given in Table 144, naphthol yellow, chrysoidine, auramine, eosin, and methylene blue may be regarded as substances giving normal electrolyte solutions. The same is true of safranine, which according to Herzog and Polotzky [3] diffuses rapidly, and according to Biltz,[4] dialyses rapidly; it is certainly true of picric acid and its salts, and probably also of methyl green. Conductivity measurements have shown that both naphthol yellow and methylene blue are practically completely dissociated.[5] Of the dyes in Table 144, Congo red (the Congo dyes generally) and night blue are pronounced colloids; further—likewise according to Herzog and Polotzsky—on the ground of very slow diffusion and absence of dialysis, azoblue and benzopurpurin. A large number of dyes were investigated by Ruhland [6] on the basis of the method of diffusion in a 20 per cent. gelatine jelly above described (p. 550). Among the basic dyes he found besides night blue (also recognized by him as a colloid),

[1] See *W. Biltz, loc. cit.* p. 549; *R. O. Herzog* and *Polotzky, loc. cit.* p. 546.

[2] Ultramicroscopic investigations of dye solutions have been carried out especially by *Rachlmann*, Physik. Zeitschr. **4**, 884 (1904); *L. Michaelis*, Deutsch. med. Wochenschr. 1904, p. 1534; Virchows Archiv, **179**, 195 (1905); *Höber* and Frl. *Kempner*, Biochem. Zeitschr. **11**, 105 (1905).

[3] *loc. cit.* p. 546.

[4] *loc. cit.* p. 549.

[5] See among others *Miolati*, Ber. d. deutsch. chem. Ges. **28**, 1696 (1895); *Hantzsch* and *G. Osswald, ibid.* **33**, 278 (1900); *Pelet* and *Wild*, Kolloidzeitschr. **3**, 174 (1908).

[6] Jahrb. f. wissensch. Bot. **46**, 1 (1908).

Victoria blue (4 R and B), Basel blue (R and BB) and gallamine blue, and among the acid dyes trisulphon violet R, brilliant Congo R, Congo orange G, dianil blue B, curcumin S, diamine pure blue, and cyanosine spritl to be completely colloidal.

It has not always been distinguished to what extent they are hydrophilic rather than hydrophobic. The sols of Congo blue and Congorubin (cf. p. 420) and those of dyes such as indigo, aniline blue, and others, which can only be obtained by the well-known method of pouring a solution of the dye in an organic liquid into water, are certainly hydrophobic. Night blue solutions are perhaps hydrophilic [1]; the surface tension is lower than that of water; they froth, they are comparatively viscous and little sensitive towards electrolytes.[2] With substances such as the Congo dyes and so on, the colloid ions are doubtless again usually more strongly hydrated than the non-dissociated dye micellæ; hence the solutions of the dye salts appear more hydrophilic than the sols of the slightly dissociated acid. The change in the surface tension and increase in viscosity is usually unimportant. The Congo dyes (the salts) are typical colloidal electrolytes, indeed Congo red was cited as an example of the appearance of the Donnan membrane equilibrium (cf. p. 553). In spite of the slow diffusion and slight or absent dialysis the conductivity is high, the molar conductivity becomes independent of the dilution at complete dissociation.

Dyes such as ponceau, methyl violet, crystal violet, rhodamine, fuchsine, new fuchsine, and others occupy an intermediate position. They diffuse more rapidly than the colloidally dissolved dyes, dialyse considerably, under the ultramicroscope one frequently sees micellæ or a plain Tyndall cone, and the number of micellæ and the Tyndall cone are usually increased by addition of electrolyte. With some dyes of this group, such as fuchsine and crystal violet, the lowering of the surface tension is definite; accordingly an adsorption of the dissolved substances takes place at the surface, and coagulation leads to the formation of solid films (cf. p. 750). These may not only be recognized by the surface solidity caused by them, but also by their photo-electric effect.[3] The conductivity of solutions of these dyes corresponds to strong or complete dissociation. Signs of sensible hydrolysis are not usually present; thus in a fuchsine solution no considerable $H^{\cdot}$ ion concentration could be detected by the method of the catalytic decomposition of diazoacetic ester.[4]

It may be asked whether in the case of these dyes a connexion exists between size of micella and colour. In particular, the change of colour shown by indicators might be brought into relation with a coagulation, when we remember how greatly the transition from red to blue in the gold sol resembles the colour change of indicators.[5] This idea is also in principle not unjustifiable; in the case of metallic sols the peculiarities of metallic absorption and reflection of light produce the observed changes of colour (cf. p. 383); but many aniline colours have in certain regions of the spectrum almost a metallic absorption and reflection.[6] When however the

[1] *Freundlich* and *Neumann, loc. cit.* p. 549.

[2] The proof is still wanting that this behaviour is not due to foreign substances such as dextrin added to the technical dye.

[3] *O. Rohde,* Ann. d. Physik (4), **19,** 935 (1906).

[4] *Pelet-Jolivet,* Bull. d. l. Soc. Vaud. d. scienc. natur. **45,** 123 (1909).

[5] *Wo. Ostwald,* Kolloidzeitschr. **9,** 92 (1911), **10,** 97, 132 (1912); Kolloidchem. Beihefte **2,** 409 (1911).

[6] *B. Walter,* "Die Oberflächen- und Schillerfarben," Brunswick, 1895.

change in the colour of an indicator is solely conditioned by the $H^{\cdot}$ and OH' ion concentration, we cannot assume flocculation. For we know no coagulation of a sol, not even of a hydrophilic sol, which is caused exclusively by $H^{\cdot}$ (and OH') ions and not also by other ions. With Congorubin, however, Wo. Ostwald,[1] and before him Schulemann,[2] have shown that the change in colour from red to blue is produced by every possible electrolyte, and that, like a gold sol, it completely obeys the laws known for the coagulation of hydrophobic sols.[3] Here it cannot be doubted that the change in colour is conditioned by a change in the size of the particles, by the association of smaller micellæ to larger ones. Schulemann's attention was drawn to the phenomenon because this dye, deposited in the organism in intravital staining, shows a change of colour which cannot be referred to a change produced by $H^{\cdot}$ or OH' ions, concerning which it could however be proved that other neutral salts also produced a similar colour change. This phenomenon, which is frequently designated by the term metachromasy, was also found by Schulemann for a number of other dyes, such as Bordeaux extra, diamine violet N, azo-blue, and benzazurine. From this it is exceedingly probable that they also behave in the test-tube like Congorubin, and that in their case as well the colour change depends upon a coagulation. With the usual indicators, such as phenolphthalein, litmus, Congo red, the colour change, on the other hand, is so decidedly a function of the $H^{\cdot}$ ion concentration, so little dependent upon other ions, that only a subsidiary rôle can be assigned to the mere change in size of particles, and a pure chemical change must be regarded as the conditioning factor.[4] It is however curious, as Zsigmondy[5] points out, that with solutions of the Congo acid all conditions which favour a dispersion of the particles, for example the use of organic solvents, such as alcohol and acetone, lead to the red colour, all that lessen dispersion to the blue. But I should prefer for the present to agree with Hantzsch's view that it is a matter of chemical isomerides. A colloido-chemical explanation of the fact that the red acid may also be obtained in the solid form is too difficult, and the proof is wanting that the change of the red acid into the blue follows the rules of coagulation in its possible dependence upon the nature of the electrolyte.

The coagulation of dye solutions by electrolytes and their mutual influence has been investigated in particular by Buxton and Teague[6] and Ruhland.[7] In general the behaviour is such as would be expected from the colloido-chemical nature of their solutions. How largely Congorubin

[1] *loc. cit.* p. 416.

[2] Biochem. Zeitschr. **80,** 1 (1917); Kolloidzeitschr. **20,** 113 (1917).

[3] It is true that, especially in dyeing with Congorubin in presence of salts and acids, some irregularities at present difficult to explain appear; *Haller* [Kolloidzeitschr. **27,** 188 (1920)] hence regards it as possible that the change of colour with acids is not completely similar in nature to that with salts, and that the impurities in the Congorubin must be taken more into account. Connected with this is, perhaps, the peculiar acceleration of the acid change of colour by electrolytes described by *Lüers* [Kolloidzeitschr. **26,** 15 (1920)].

[4] See on this point also *Hantzsch*, Ber. d. deutsch. chem. Ges. **46,** 1537 (1913); **48,** 158 (1915); Kolloidzeitschr. **15,** 79 (1914); Zeitschr. f. Elektrochemie, **20,** 480 (1914); *K. Voigt*, Kolloidzeitschr. **15,** 84 (1914); *Kruyt* and *Kolthoff*, *ibid.* **21,** 22 (1917); Pihlblad, Zeitschr. f. physik. chemie, **81,** 417 (1913).

[5] "Kolloidchemie," 3rd Edition, p. 318.

[6] Zeitschr. f. physik. Chemie, **60,** 469, 489 (1907).

[7] *loc. cit.* p. 650.

solutions correspond to the hydrophobic sols has already been discussed above (p. 420). This is also true of solutions of Congo red, benzopurpurin and others ; since they give negative sols, the adsorbability and valency of the kations play the chief part. Frequently the differences between ions of different valency are not so great as with most hydrophobic sols, and alkali salts only flocculate at fairly high concentrations, so that the behaviour recalls that of the Odén sulphur sols. It is often observed that electrolytes, without completely flocculating, coarsen the particles greatly, so that the originally amicronic dye solution becomes submicronic. Acids and alkalis only precipitate non-colloidal dye solutions (such as those of eosin, safranine, methylene blue, and others) in so far as they form a difficultly soluble dye acid or dye base, while acid dyes remain dissolved in alkaline solution, and basic ones in acid solution, even at high concentrations. It corresponds with the colloidal nature of night-blue solution that, although it is a basic dye, it is coagulated by acids. Ruhland investigated the coagulation of a large number of dyes, but only by two electrolytes ($CaCl_2$ and $NiCl_2$), in different concentrations. He confirms in general the results just discussed, namely, that dyes which diffuse slowly into a gelatine gel are, as a rule, coagulated in low concentrations ; diamine pure blue forms an exception, being only weakly coagulated by $CaCl_2$, although, according to diffusion experiments, its solutions are colloidal. Perhaps this is due to a hydrophilic behaviour of this solution, unless it arises from the basic dye being only weakly flocculated by the univalent Cl' ion.

The mutual coagulation of two dye solutions follows to a large extent the rule (cf. p. 477) that oppositely charged sols mutually coagulate ; hence acid dyes act upon basic and *vice versa*. A middle flocculation zone and an upper non-flocculation zone are quite distinctly observed (as in the interaction of hydrophobic sols), in the latter of which, therefore, the dye in excess reverses the charge of the particles of the other. Buxton and Teague point out the rule that the colloidal nature of the dye solution produces its effect upon the breadth of the flocculation zone. Two strongly colloidal dye solutions, such as night blue + Congo red, show a sharp flocculation zone. A slight excess of one or the other dye causes a reversal of charge and peptization. In all other cases the flocculation zone is broader, since a considerable excess of a solution which is less distinctly colloidal is necessary to reverse the charge and to peptize. In two slightly colloidal or non-colloidal dye solutions the coagulation is usually incomplete. The difficultly soluble salt of dye acid + dye base separates out, and a large excess of the one dye is necessary to completely peptize the flocculi.

A protective action of the dyes such as that discussed in the case of hydrophilic sols (cf. p. 589) has not yet been observed, and is perhaps not to be expected, since they are too hydrophobic in character. But in given circumstances they are certainly able to act protectively, because thanks to their adsorption they impart a charge. This explains the protective action of erythrosine upon AgBr sols and suspensions, observed by Lüppo-Cramer,[1] and more closely investigated by Miss Stevenson.[2] Erythrosine must according to its diffusion and dialysis be regarded as a practically truly dissolved dye. Accordingly no protective action on a gold sol is observed. That it acts so distinctly protectively upon a AgBr sol depends upon the fact that it charges up sensibly ; the kataphoretic migration velocity of the sol containing dye is 30 per cent. greater than that free from

[1] "Photographische Probleme," Halle, 1907, p. 28.
[2] Kolloidzeitschr. **10**, 249 (1912).

dye. The adsorption of the dye upon the AgBr particles was abundant and easily measurable. An ultramicroscopic count of the particles showed that their number had not been seriously increased by the dye. Hence no subdivision worth mentioning had taken place. This is a good example of how greatly the charging up of the micellæ, the growth of the electrokinetic P.D. ζ up to the maximum of the ζ, c curve (cf. p. 258) can increase the stability of a sol.

The adsorption of a dye on different adsorbents, which has already been frequently touched upon (cf. p. 202), will be again discussed in detail later (p. 753).

Non-aqueous Lyophilic Sols

Lyophilic Sols in Organic Dispersion Media

During the discussion of lyophobic sols in non-aqueous dispersion media it was incidentally emphasized how little is known concerning their conditions of stability, and that it is therefore more or less arbitrary whether they are included among the lyophobic or lyophilic sols. If in the following pages non-aqueous sols containing as disperse phase a substance which gives a lyophilic sol when colloidally dissolved in water are also in part regarded as lyophilic sols, this view is perhaps fundamentally incorrect, for it is quite possible, if not probable, that substances which are so hydrophilic as to give hydrophilic sols, for this very reason are lyophobic towards organic solvents and give lyophobic sols in them. It is true that glycerine with its high dielectric constant is in many respects so nearly related to water that the substances which dissolve in water to hydrophilic sols will also give lyophilic sols in glycerine. Th. Graham[1] prepared colloidal solutions of silicic acid in glycerine, alcohol, and concentrated sulphuric acid: the glycerosol, by heating a gel of silicic acid with glycerine, an alcosol by adding alcohol to an aqueous silicic acid sol and then dialysing against alcohol. The alcosol is insensitive to water, electrolytes, and solid powders, but gelatinizes upon concentration.

How largely peptization by another dispersion medium depends upon whether the substance acting as protective colloid is to a certain extent soluble in the dispersion medium may be seen from the following observation of L. Wöhler.[2] The red platinum sol protected by stannic acid (p. 598) is soluble in ethyl ether and acetic ester. It may be shaken out with them. This appears at first very astonishing, since stannic acid is insoluble in these liquids. But Wöhler was able to show that it is not the stannic acid that acts as protective colloid, but the $SnCl_4$, which is soluble in these liquids, or a basic salt $SnCl_3OH$; if the sols in question are prepared with careful exclusion of chlorine or more generally halogen compounds, the platinum protected by stannic acid was insoluble in the organic liquids named. Chlorine and bromine compounds were necessary for the formation of the protected platinum soluble in the organic liquids.

If in the case of a protective action an affinity between the protecting substance and the dispersion medium is necessary, on the other hand we may obtain colloidal solutions of substances in non-aqueous dispersion media on account of their lower solubility and velocity of crystallization, although these substances do not give such solutions in water, since in the latter they become too coarse and separate out. Upon this fact doubtless depends the stability of the organosols of carbonates investigated by

[1] Pogg. Ann. **123**, 529 (1864).
[2] Kolloidzeitschr. **7**, 247 *et seq.* (1910).

Neuberg.[1] He passed CO_2 into methyl-alcoholic solutions of CaO, BaO, MgO, and obtained viscous solutions of the carbonates, which could be mixed with organic liquids such as ethyl ether, chloroform, benzene, etc. Sulphuric acid and phosphoric acid precipitated gelatinous sulphates and phosphates from them.

Gelatine also dissolves in glycerine to a sol. Arisz [2] examined its properties in detail. As it was here, however, mainly a matter of the sol-gel transformation, these results will be dealt with later (p. 701).

Other organic substances, which give colloidal solutions not only in water but in organic solvents, are the lecithins, cephalins, and related substances. This was proved for solutions of lecithin, cephalin, and the like in chloroform, petroleum ether and other solvents by S. Loewe,[3] after Porges and Neubauer [4] had pointed out that the precipitation of lecithin in ethyl alcohol solution by $CdCl_2$ and other salts had many points of similarity with a coagulation by electrolyte, and that the ethereal solution also has properties which may be interpreted on the assumption of colloidal solution. According to Loewe cholesterol, on the other hand, is truly dissolved in chloroform and other solvents. The solutions of the other substances named may, according to Loewe, be resolved under the ultramicroscope, and they give a much smaller depression of the vapour pressure than corresponds to the molecular weight calculated from the formula.[5]

Connected with the colloidal character of these solutions is their power of taking up substances which the pure dispersion medium takes up but slightly or not at all. Thus methylene blue and other dyes do not dissolve in chloroform, but do so in a chloroform sol of cephalin. This taking-up is similar to an adsorption, the isothermal holds.[6] The experiments were carried out by placing a layer of aqueous methylene blue on a solution of cephalin, and allowing them to come into equilibrium ; they must not be shaken, since otherwise very permanent emulsions are formed. It is almost certain that the micellæ formed in organic dispersion media also contain water as well as cephalin. The amount of dye taken up is greater, however, than if it were only a question of fine drops of the dye solution. Hence an adsorption must be assumed. Concerning the nature of these micellæ some experiments by Freundlich and Gann [7] afford further information. They found that pure fats form true solutions in chloroform, as also does spermaceti. But when the presence of soap was ensured by treatment with alkali, a dense emulsion of spermaceti in chloroform, in which the particles were in part submicrons, was formed. These micellæ had a composition

Spermaceti
Soap
Water

[1] Ber. d. Berl. Akad. d. Wiss. **45**, 820 (1907) ; *Neuberg* and *Neimann*, Biochem. Zeitschr. **1**, 166 (1906) ; *Neuberg* and *Rewald*, Kolloidzeitschr. **2**, 321 and 354 (1908).

[2] Kolloidchem. Beiheft **7**, 1 (1915).

[3] Biochem. Zeitschr. **42**, 207 (1912).

[4] Kolloidzeitschr. **5**, 193 (1909).

[5] *S. Loewe* determined the lowering of the vapour pressure by the microscopic method by *Barger* [Journ. Chem. Soc. **84**, 286 (1904), Barger and Ewins, *ibid.* **87**, 1756 (1905)] ; in this the growth or diminution of a drop of the solution as compared with a drop of solution of known molar concentration is determined. The boiling-point method fails for the same reason as with soap solutions (cf. p. 567). For an improvement of the *Barger* method see *Rast*, Ber. d. deutsch. chem. Ges. **54**, 1979 (1921).

[6] *S. Loewe*, Biochem. Zeitschr. **42**, 150 (1912).

[7] *loc. cit.* p. 605.

This spermaceti milk was again able to adsorb methylene blue abundantly, while the solution of pure spermaceti only dissolved very little of it. Perhaps the presence of soap-like decomposition products is also important in the case of lecithin and cephalin for the production of their colloidal solutions in organic dispersion media. Connected with the adsorptive power and the water content is the fact, pointed out by Porges and Neubauer,[1] that ethereal solutions of lecithin are also able to dissolve all sorts of substances (glucose and the like) which are not soluble in ether. Here also belongs the phenomenon described by Haller[2] that dyes such as fuchsine, Nile blue, and others, which do not dissolve in xylene, appear to do so when adsorbed in higher fatty acids; micellæ could again be seen ultramicroscopically.

Allied to these sols are the sols which can be formed in alcoholic mastic solutions by addition of water.[3] They deserve to be systematically investigated, especially the transition to the sols containing much water. For while the alcoholic sols just mentioned appear to have a lyophilic character, the mastic hydrosols obtained by pouring an alcoholic mastic solution into an excess of water are entirely hydrophobic. Conversely, the addition of alcohol to an aqueous gelatine sol appears to give it a more lyophobic character.[4]

The sols hitherto discussed have an unmistakably lyophilic character. On the other hand, according to an observation by Brailsford Robertson,[5] we appear to have a case of a substance forming a lyophilic sol in water giving a more lyophobic alcosol. If salmine sulphate (a protamine salt) is washed out with alcohol by suspending it therein three or four times, it finally remains peptized as a fairly stable suspension.

That many substances which dissolve to hydrophilic sols in water, such as soaps, saponins, tannins, dyes, etc., form true solutions in other liquids, has already been discussed earlier, p. 559.

Metallic Sols in Molten Salts

A noteworthy group of sols has been investigated by R. Lorenz and his co-workers[6]; he describes them as *pyrosols*.

The melts of a series of metallic salts readily become turbid under conditions under which one is compelled to assume finely divided metal as the cause. If $PbCl_2$, as pure and dry as possible, be melted, and metallic lead be heated in the melt, it is observed that dark clouds are explosively thrown from the drops of lead into the melt, and render it turbid. That these clouds consist of finely divided metal is rendered probable by the following experiment.

Cadmium boils at 780°. This boiling-point lies between the melting-point 570° and the boiling-point 960° of its chloride; cadmium may therefore be heated above its boiling-point under molten cadmium chloride.

[1] *loc. cit.* p. 655; there also a discussion by *P. Mayer*, Biochem. Zeitschr. **4**, 545 (1907); *Bing*, Skand. Arch. f. Physiol. **9**, 336 (1899).

[2] Kolloidzeitschr. **22**, 127 (1918).

[3] *J. Friedländer*, Zeitschr. f. physik. Chemie, **38**, 432 *et seq.* (1901); *Wo. Ostwald*, Kolloidzeitschr. **1**, 335 (1907).

[4] *Scarpa*, Kolloidzeitschr. **15**, 8 (1914).

[5] Journ. Phys. Chem. **16**, 385 (1912).

[6] For a comprehensive description see *R. Lorenz*, Kolloidzeitschr. **18**, 177 (1916); further *R. Lorenz*, "Die Elektrolyse geschmolzener Salze," Halle, 1905, II, p. 32 *et seq.*; *R. Lorenz* and *Kaufler*, "Elektrochemie geschmolzener Salze," Leipzig, 1909.

A quite continuous change in the behaviour is now observed. Even below the melting-point brown mists of the metal are forced out into the melt; this formation of mist increases as the boiling-point of the metal is approached, and when it has been reached or passed, the metal boils through the melt and condenses outside on colder parts of the vessel.

In the electrolysis of molten salts the conditions at the cathode are obviously favourable for the formation of this mist. Faraday and Bunsen had already in fact described a turbidity and reduction of the melt in the case of such electrolytes. It is true that R. Lorenz proved that when oxygen and water are present in the electrolyte, the burning of the metal or hydrolytic reactions may cause various other phenomena to appear, which likewise lead to a turbidity. But he found that even in absence of air and with perfectly dry electrolytes the metallic mist was nevertheless given off at the cathode. Reducing agents such as KCN also produce turbidity in molten salts.

Lorenz [1] has not yet succeeded in examining the turbid melts themselves in the ultramicroscope, but only the turbid crystals to which they solidify. This gave the following result. From molten $PbCl_2$, AgCl, and AgBr optically empty crystals may be obtained. Particular precautions must be taken; with the chlorides a perfectly dry stream of chlorine and HCl gases must be led through the melt, with bromides bromine must be employed, and the melt then allowed to solidify rapidly in the air. The grey or brown crystals, on the other hand, which are obtained from the pyrosols, are not optically empty, but are rich in submicrons. Hence it can scarcely be doubted that these submicrons were also present in the melt.

The fact that it is necessary to cool quickly in order to obtain optically empty crystals, while with slow cooling the crystals are always somewhat turbid, suggests that the state of complete purity does not correspond to equilibrium, but rather that a certain dissociation takes place in the case of $PbCl_2$, perhaps according to the equation

$$n\mathrm{PbCl_2} = (n - 1)\,\mathrm{PbCl_2} + \mathrm{Pb} + \mathrm{Cl_2},$$

and the lead separated is contained with $PbCl_2$ in a micella

$$\left|\begin{array}{c}\mathrm{Pb}\\(n-1)\mathrm{PbCl_2}\end{array}\right|$$

With thallous chloride equilibrium is set up so readily and quickly that optically empty crystals cannot be successfully obtained; possibly a part of the salt is oxidized thereby to thallic chloride according to the equation

$$n\mathrm{TlCl} = (n - 3)\,\mathrm{TlCl} + 2\mathrm{Tl} + \mathrm{TlCl_3}.$$

Since apparently well defined equilibria exist between micellæ and intermicellar liquid, these sols have here been included among the lyophilic; for it is with these that direct interaction with the dispersion medium should condition the stability. In favour of this view we have the further fact that salts such as KCl, which form double salts with $PbCl_2$, and hence saturate its residual valencies, destroy the pyrosol and flocculate the lead. Small concentrations of KCl are not sufficient for this, as in the coagulation of hydrophobic sols: considerable concentrations are necessary, as with salting out, since the residual valencies of a large number of the molecules of the melt must be saturated. Conversely, KCl hinders, as its concen-

[1] *R. Lorenz* and *Eitel*, Zeitschr. f. anorg. Chemie, **91**, 46, 57, 61 (1915).

tration increases, the formation of mist by the action of lead upon the $PbCl_2$ melt, and the decreasing affinity between melt and metal appears in the fact that the interfacial tension between lead and melt increases with increase of KCl content. This is a good example of the view repeatedly emphasized (cf. p. 234) that an increasing tendency to saturate residual valencies, strong adsorption and falling interfacial tension go parallel with one another, as do also decreasing tendency to saturate residual valencies, weak adsorption, and increasing interfacial tension.

The turbid melts of AgCl and AgBr, containing colloidally dissolved silver, deserve particular attention. Lorenz[1] was able to show that these are, in fact, the photochlorides, which are so important for the theory of the latent image in photography (cf. p. 803).

II. GELS

Very considerable difficulties are met with in trying to define a gel. A certain tendency existed and perhaps still exists to call everything which separates from a sol in solid form, unless it be coarsely crystalline, a gel. I agree with Weissenberger[2] in considering this inexpedient, and would prefer to employ the expression Coagel. Hence flocculi poor in liquid, or microcrystalline powders, such as usually separate from metal or sulphide sols, will not be described as gels in the following pages. On the other hand, Miss Laing and McBain[3] desire to limit the conception of a gel very narrowly. They found that the transparent jellies to which soap solutions may set do not differ in the slightest degree in a whole series of properties (vapour pressure, conductivity, etc.) from soap sols of the same content and temperature, while the opaque " gels " containing coagulated soap, which may arise from the sols or transparent jellies, are entirely different from these in all their properties. They would like to call the jellies, which differ from sols only in their elastic properties, gels, and not the " gels " which contain coagulated soap. One can say already that a number of real gels, such as gelatine jellies and the jellies from protein sols, would come under this limited definition of Miss Laing and McBain; available data already allow of the conclusion that, in the case of these sols and gels also, almost all properties are the same, and that they differ essentially only in their elastic properties. But we can also now say that other completely transparent amorphous jellies would not then be included among the gels, thus for instance the jellies into which Al_2O_3 and CeO_2 sols are transformed. This transformation proceeds according to the same laws which govern the flocculation of an amorphous or microcrystalline powder from a gold or CuO sol. One can hardly assume that the Al_2O_3 or CeO_2 gels are completely like the sols from which they are formed. Also in the case of that prototype of a gel, silicic acid, this is entirely questionable.

In the following pages I shall therefore employ the conception of a gel in a somewhat wider sense than do Miss Laing and McBain, namely to colloidally disperse structures consisting of a solid and a liquid phase or perhaps also of two viscous liquid phases, and having shape and cohesion, that is, elastic properties, although it may be very rich in liquid. I shall also include structures such as the crystals of many proteins, or starch

[1] Zeitschr. f. Elektrochemie, **7**, 277 (1900); *R. Lorenz* and *Hiege*, Zeitschr. f. anorg. Chemie, **92**, 27 (1915).
[2] Kolloidzeitschr. **25**, 230 (1919).
[3] Journ. Chem. Soc. **117**, 1506 (1920).

grains and fibres, which undergo imbibition and swelling, and likewise the jelly-like masses which may be formed under certain conditions by chemical action upon crystalline silicates, aluminates and other substances. This is done with the consciousness that among the structures thus classed in one group it may later be necessary to distinguish sharply between special cases.

As we have said, it is assumed that gels are polyphasic. In this respect alone opinions already differ. There are investigators who prefer to regard them as monophasic.[1] This appears to me artificial and unpractical. In many cases ultramicroscopic investigation teaches us that the gels are optically heterogeneous. And where this is not the case, they have usually been formed from sols which have been proved to be heterogeneous in very different ways. It may be confessed that the idea of a phase can be formed in such a way that even coarsely heterogeneous structures may be regarded as monophasic[2]; but I regard the value of such a forced view as slight. For in these structures are observed in a pronounced degree adsorption phenomena, ageing processes, and so on, processes which are readily understood under the assumption of more than one phase. And that the single micella must then sometimes count as a large molecule, does not appear to me to be at all open to objection. With large molecules loose attachments by residual valencies with retention of the rest of the structure, that is to say adsorption, may occur as at the interface of two phases.

The majority of investigators also consider gels as polyphasic. But clear agreement does not exist as to the nature of the polyphasic structure. Up to a few years ago the view based on the work of Bütschli[3] was very general, that gels consist of submicronic walls of amorphous solid substances or highly viscous liquids, which enclose microscopic drops of liquid. Later ultramicroscopic investigations by Zsigmondy and his co-workers[4] have not confirmed this honeycomb theory of gels. On the contrary they came to the conclusion that the gels examined by them were, so to speak, ultramicroscopic doughs; a mass of micellæ separated by submicronic or amicronic films of liquid. According to Bütschli the liquid is the disperse phase, the amorphous solid the dispersion medium. According to Zsigmondy, on the other hand, the amorphous solid is, as with the sols, disperse phase, and the liquid dispersion medium, only that in contrast to the sols the liquid does not greatly preponderate in amount, but only suffices to separate the micellæ from one another by fine films. The experiments of Miss Laing and McBain, already mentioned, on transparent soap jellies led to the same result (cf. p. 658). In these cases the results seem to me so definite, that I do not doubt the correctness of the view described. The only question is whether we are right in extending them without further consideration to all gels, or whether there may not be some for which the

[1] *Katz*, Kolloidchem. Beihefte **9**, 1 (1917).

[2] See *Büchner, loc. cit.* p. 362.

[3] "Untersuchungen über mikroskopische Schäume und die Struktur des Protoplasmas," Leipzig, 1892; Verhandl. d. naturhist.-mediz. Ver. z. Heidelberg, N.F., **5**, 230, 360 (1894–95); Abhandl. Heidelb. Ges. d. Wiss. **40**, 1 (1896); "Untersuchungen über Structuren," Leipzig, 1898; "Untersuchungen über Mikrostructuren des erstarrten Schwefels," Leipzig, 1900; Verhandl. d. naturh.-med. Ver. z. Heidelb. N.F., **6**, 287 (1900); Sitzungsber. d. Kgl. Bayr. Akad. d. Wiss. **33**, 215 (1903). See a summary of *Bütschli's* work in Die Naturwissenschaften, **8**, 567 (1920).

[4] *Zsigmondy*, Zeitschr. f. anorg. Chem. **71**, 356 (1911); *Bachmann, ibid.* **73**, 125 (1911), **79**, 202 (1912); *Zsigmondy*, Phys. Ztschr. **14**, 1098 (1913); see also an observation made in *Zsigmondy's* laboratory by *Menz* [Ztschr. physik. Chem. **66**, 137 (1909)].

honeycomb theory holds. With the consciousness that this generalization is not perhaps entirely justified, the Zsigmondy theory will for the present be assumed to apply to all gels.

A comprehensive survey of the general properties of gels is difficult until their structure and the behaviour connected with it have been considered more closely. Hence the results of the ultramicroscopic examination of gels, the taking-up and giving-up of liquid, and the sol-gel transformation will first be discussed in detail.

The Behaviour of Gels under the Ultramicroscope

Among the gels whose structure has been largely elucidated are, in particular, the well-known gels of gelatine and agar, to which the concentrated sols of these substances set, and various silicic acid gels; namely, those prepared artificially in the usual way from sodium waterglass solution and hydrochloric acid, which may be purified by dialysis both before and after gelation, and further some naturally occuring silicic acid gels, the mineral hydrophane, and tabaschir, which is derived from the vegetable kingdom. Tabaschir is formed from a liquid containing silicic acid which is present in the internodial hollows of the bamboo cane (*Bambusa arundinacea*), and which dries first to a jelly and finally to a solid. It is perhaps useful to describe gels formed by drying, and very poor in liquid but nevertheless coherent, as *xerogels*. Xerogels, such as the dry silicic acid jelly or tabaschir, may also be easily soaked through with liquids other than water (alcohol, benzene, etc.).

Bütschli [1] examined both natural and artificial silicic acid gels under the microscope. The dry gel as well as that filled with liquid is transparent and optically empty under the microscope. Upon saturating a dry silicic acid gel, as also upon drying a saturated gel, an opacity-point [2] is observed; the originally transparent gel becomes opaque, indeed chalk-white, and only when fully dried or fully saturated again, as the case may be, does it again become transparent. In the region between the opacity-points a fine honeycomb-like structure is observed under the microscope, which with volatile liquids appears very variable. Bütschli was able to stabilize and photograph it by soaking the gel in a mixture of a non-volatile and a volatile liquid, such as cedarwood oil and chloroform, and allowing the volatile liquid to evaporate. He assumed that the fine structure observed is to be ascribed to the gel; it would then have cavities of 1–1·5 μ diameter, which in the saturated state are filled with liquid, and honeycomb walls the thickness of which might be estimated under the microscope at 0·2 to 0·3 μ. Since these are thickened by the non-volatile liquid, Bütschli assumed that the thickness of the wall is in reality considerably smaller than this, hence of about ultramicroscopic fineness.

These results could not be confirmed by Zsigmondy [3] in his ultramicroscopic examination of the silicic acid gels. The dry gels, and also those filled with liquid, were mostly optically empty; only a few isolated submicrons could be seen. Upon drying the gel there appeared in the region between the opacity-points a weak Tyndall cone, which was unmistakable from its state of polarization and continuously increased in strength as drying proceeded. Gradually a profusion of densely packed and, in part,

[1] Verh. d. naturh.-med. Ver. z. Heidelberg, N.F., **6**, 287 (1900).
[2] In the German "Umschlag"; no English equivalent appears to exist yet.
[3] Zeitschr. f. anorg. Chemie, **71**, 356 (1911); *Bachmann, ibid.* **73**, 163 *et seq.* (1911).

strongly illuminated submicrons appeared; these faded again, on further drying, to a Tyndall cone, until the field became optically empty with the dry gel. The structure is therefore much finer than that assumed by Bütschli; Zsigmondy rightly points out that with cavities of 1–1·5 μ diameter filled with air the dry gel should show up brightly under the ultramicroscope on account of such great heterogeneity. With ordinary illumination it should appear white, not transparent. The appearance of the strong Tyndall cone and a profusion of submicrons during the opacity-stage unquestionably corresponds to the honeycomb structure already recognized by Bütschli under the microscope. But it obviously does not belong to the gel as such, but on the evaporation of the liquid during drying an abundance of the finest gas bubbles are formed, which fill, not single cavities, but a larger connected network of ultramicroscopic canals. The difference in refractive index between the gel space filled with gas and that still filled with liquid is so great, that this fine foam produces the microscopic and ultramicroscopic effects described. Fig. 124 gives a picture of this state and at the same time an idea of how the foam of gas bubbles temporarily produced during drying is superimposed upon the actual fine-structure of the gel.[1]

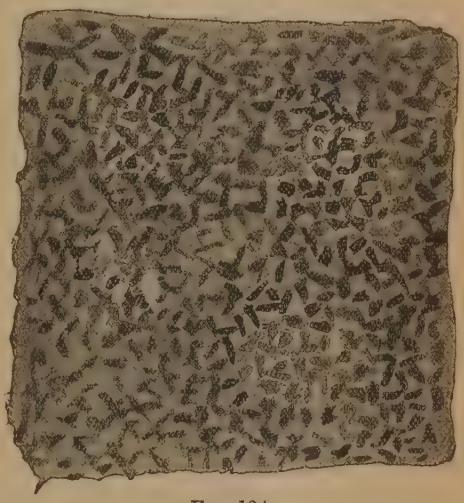


Fig. 124.

This view of the structure of the gel was supported by Bachmann's experiments.[2] He followed ultramicroscopically the gelation of silicic acid, gelatine, and agar sols. The process proceeded in the case of a 1 per cent. gelatine solution in the following stages. The original sol only showed a Tyndall cone. Then a strong flicker appeared in it; this finally resolved itself into a crowd of submicrons, which carried out lively translatory movements. The greater their number became, the more viscous became the liquid, which was also evident from the fact that larger particles of dust first exhibited an oscillatory instead of a translatory movement, and finally none of recognizable magnitude. Also in the case of the submicrons the movement passed from a translatory to an oscillatory one and finally ceased to be evident, a sign that the sol had set to a gel. At this concentration the sol did not set uniformly to a gel, but large gel flocculi separated, which in spite of their size emitted normal Tyndall light, since they were composed of submicrons and amicrons. It is noteworthy that the gels formed from more concentrated solutions (over 2 per cent.) were much less or not at all resolvable under the ultramicroscope; only the polarization of the Tyndall light emitted betrayed the heterogeneity. In conformity with

[1] Further matter concerning the interpretation of the Bütschli structures in Bachmann, Zeitschr. f. anorg. Chemie, **73**, 125 (1911).

[2] *loc. cit.* p. 659.

this ultramicroscopic behaviour dilute gels appear more cloudy than concentrated ones.

Agar and silicic acid gels behaved quite similarly. Bachmann [1] points out that "this agreement is so striking that it is almost impossible to decide by ultramicroscopic observation whether we are dealing with a liquid [2] silicic acid or a gelatine jelly. Equally concentrated silicic acid and gelatine jellies (content 1 to 3 per cent.) may be distinguished ultramicroscopically after some practice by the silicic acid appearing more clearly differentiated." This is particularly emphasized, since silicic acid and gelatine gels may be taken as typical of the contrast between inelastic and elastic gels (cf. below).

From these experiments of Bachmann follows the grained structure of gels; not honeycomb walls, which surround ultramicroscopic drops of liquid, but an abundance of amicrons or submicrons, which are distributed in the liquid as dispersion medium. In favour of this view we have also especially the fact that gels can be saturated in the course of minutes by liquids. In the case of a structure such as the xerogel of silicic acid one would expect a much longer time to be required for a liquid such as benzene to penetrate the innumerable silicic acid layers of a honeycomb structure.

The proof given by Zsigmondy and Bachmann of a granular fine-structure for gels is, by the way, nothing less than a confirmation of Nägeli's [3] micellar theory of gels. He also assumed that solid micellæ are separated by extremely fine films of liquid.

Absorption and Loss of Liquid by Non-elastic Gels

As remarked above, it is useful to distinguish between *non-elastic* and *elastic gels*. As prototype of the non-elastic we may take a silicic acid gel. When freshly prepared from the sol it has a volume which decreases upon drying; but the decrease rapidly attains a limit, from which onwards air takes the place of liquid in the cavities of the gel. The opacity-point already mentioned occurs. The volume is practically retained unaltered until the gel is completely dry. If it then again takes up liquid, this only fills the cavities without increasing the volume of the gel. Of other gels, those of stannic acid and other metallic oxides belong in particular to this group.

The counterpart of this is the gelatine gel. Upon drying, the volume decreases continuously, until we finally have the horn-like plate of gelatine. If this again takes up liquid, it increases greatly in volume, and may attain a size which does not differ greatly from the gel obtained immediately after separation from the sol. The gel *swells*. We may thus distinguish between *swelling* and *non-swelling* gels.

The absorption and loss of liquid by non-elastic gels will first be discussed, not because it is particularly simple fundamentally—on the contrary, with some elastic gels it is probably less disturbed by subsidiary causes, hysteresis phenomena, and the like—but from the behaviour of the non-elastic gels conclusions may be drawn as to the size of the cavities in gels, so that they supplement in a quantitative manner the results of the foregoing section. The absorption and loss of water by gels is followed by means of the vapour pressure possessed by the gel with different liquid content.

[1] Zeitschr. f. anorg. Chemie, **73**, 158–9 (1911).
[2] Should be "saturated with liquid."
[3] "Theorie der Gärung," München, 1879, p. 121 *et seq.*

Van Bemmelen [1] already carried out extensive and careful experiments of this kind especially on silicic acid gels and water, which Zsigmondy and his co-workers [2] have extended on this and other gels and with other liquids. Van Bemmelen worked with desiccators in which the gel was placed over mixtures of H_2SO_4 and water of various concentrations. The equilibria were set up very slowly, often only in the course of months. Zsigmondy reduced the time required considerably and avoided the influence of air by carrying out the experiments in a vacuum in vessels as small as possible. Since the vapour pressure isothermal is one of the chief characteristics of a gel, the experimental arrangement in its simplest form may be described. In A (cf. Fig. 125) is placed the liquid which communicates its vapour pressure to the space. For water, solutions of sulphuric acid in water are used, for alcohol solutions of alcohol in glycerine, for benzene solutions of benzene in paraffin oil. B is the manometer, D the vessel containing the gel, which is taken off from time to time in order to determine its weight and hence that of the amount of liquid taken up by the gel. Evacuation takes place through H, a calcium chloride tube being interposed.

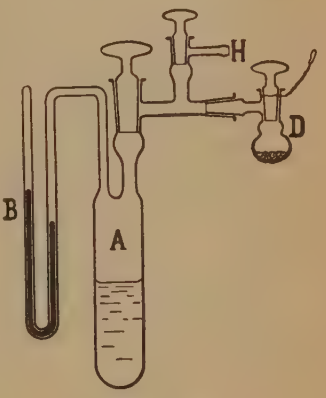


Fig. 125.

A gel freshly separated from a water-glass solution by hydrochloric acid at first contains the water so loosely bound that its vapour pressure cannot be distinguished from that of pure water; the rate of evaporation of water from the gel is consequently practically equal to that of pure water. This remains so until about 100 millimols of water are associated with 1 gram of SiO_2. In this region the gel is very rich in water, the liquid may be pressed out by the slightest pressure. Upon further loss of water the vapour pressure commences to fall. This is explained according to Zsigmondy's theory of gels [3] by the water commencing to evaporate from the capillaries of the gel; in these the liquid is bounded by concave menisci, which, corresponding with the fineness of the capillary spaces, have very small radii of curvature. As is well known (p. 45), liquids evaporate with smaller vapour pressures from such concave menisci than from a plane liquid surface. If the micellæ were so far solidified that they no longer changed, the diameter of the capillary spaces would be constant, and the vapour pressure would be lower than the saturation pressure by a constant or only slightly variable amount. This is, however, not the case; the pressure falls at first fairly sensibly

[1] Zeitschr. f. anorg. Chemie, **5**, 466 (1894) (CuO); **13**, 233 (1897); **18**, 14, 98 (1898); **30**, 265 (1902) (SiO_2; these papers are particularly important); in common with *Klobbie*, Journ. prakt. Chemie, **46**, 497 (1892) (Fe_2O_3); Zeitschr. f. anorg. Chemie, **49**, 125 (1906) (ZrO_2); Rec. d. Trav. chim. d. Pays-Bas, **7**, 37 (1888) (SiO_2, SnO_2, Al_2O_3, Fe_2O_3, Cr_2O_3).

[2] *Zsigmondy*, Zeitschr. f. anorg. Chemie, **71**, 356 (1911); Physik. Zeitschr. **14**, 1098 (1913); *Zsigmondy, Bachmann* and Miss *Stevenson*, Zeitschr. f. anorg. Chemie, **75**, 189 (1912); *Bachmann, ibid.* **79**, 202 (1912); *J. S. Anderson*, Zeitschr. f. physik. Chemie, **88**, 191 (1914).

[3] *loc. cit.* p. 659.

according to the part AO of the curve (Fig. 126), because the micellæ are still so rich in water that they too give off water and the total volume of the gel still decreases; the diameter of the capillaries is thereby diminished.

At the opacity point O—about 31 millimols H_2O to 1 gram SiO_2—turbidity of the gel begins, that is, the micellæ are now so poor in water and so rigid, that they no longer follow a further decrease in water content; the capillary volume remains constant, air or gas bubbles appear. The capillary diameter, and hence the vapour pressure, should now remain practically constant as long as liquid evaporates from the capillaries, provided that the capillaries have approximately equal diameters. In the measurements of van Bemmelen this was true to a large extent: the section

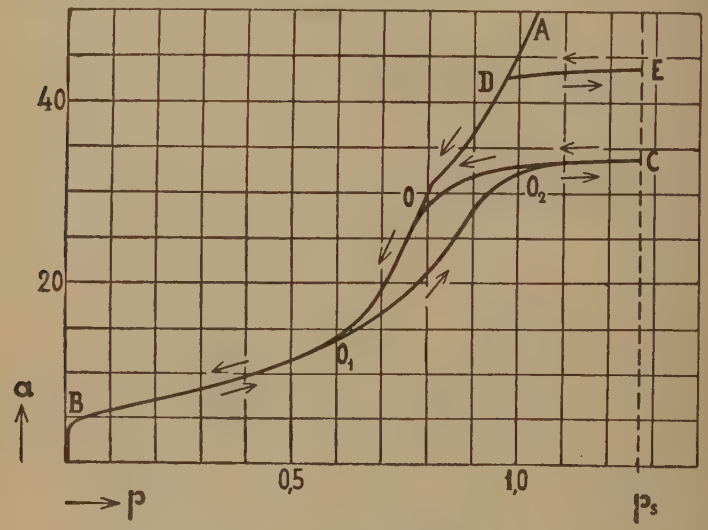


Fig. 126.—Vapour-pressure Isothermal of SiO_2 Gel.

OO_1 of the curve, the region between the opacity-points, fell vertically. In the experiments of Anderson [1] considered in Fig. 126, this was not the case. The piece OO_1 had a certain inclination to the vertical; probably the capillaries had not strictly equal diameters, and at O the water evaporates from the widest, and at O_1 from the narrowest.

From the difference between the vapour pressure p_w of this point O (or O_1 respectively) and the saturation pressure p_s at the temperature of experiment, the radius of curvature of the meniscus and hence the radius of the capillaries may be calculated from

$$r = \frac{2\sigma\varrho_d}{p_s\varrho_h \log\frac{p_s}{p_w}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The two quantities coincide provided that the thickness of the adsorption layer is not too large a fraction of the diameter of the capillaries. Equation (1) follows from equation (2), p. 45, if we substitute $\frac{p_s}{\varrho_d}$ for $\frac{RT}{M}$ and take

[1] *loc. cit.* p. 663.

nto account that here $p_\omega < p_s$, since we are dealing with a concave meniscus. The value of the vapour pressure in the region between the opacity-points s so important for the determination of the capillary radii in gels, that n Table 169 are given the r values calculated by Anderson by means of ormula (1) for various values of p_ω for water, alcohol and benzene.

TABLE 169

Vapour Pressure and Capillary Radius

t = 15°

Water. σ = 73·26. ρ_d = 1·274 × 10⁻⁵ ρ_β = 0·99913 p_s = 1·27 cm. Hg.		Alcohol. σ = 23·09 ρ_d = 8·362 × 10⁻⁵ ρ_β = 0·797 p_s = 3·26 cm. Hg.		Benzene. σ = 29·51 ρ_d = 2·609 × 10⁻⁴ ρ_β = 0·884 p_s = 6·9 cm. Hg.	
p_ω (*cm. Hg.*).	r (in $\mu\mu$).	p_ω (cm. Hg.).	r (in $\mu\mu$).	p_ω (cm. Hg.).	r (in $\mu\mu$).
0·4	0·954	1·0	0·942	0·6	0·944
0·5	1·182	1·2	1·114	1·0	1·213
0·55	1·317	1·3	1·212	1·2	1·351
0·6	1·470	1·4	1·317	1·4	1·494
0·65	1·646	1·5	1·435	1·6	1·645
0·7	1·850	1·6	1·564	1·8	1·806
0·75	2·093	1·7	1·710	2·0	1·979
0·8	2·385	1·8	1·875	2·2	2·167
0·85	2·746	1·9	2·064	2·4	2·373
0·9	3·200	2·0	2·279	2·6	2·601
0·95	3·796	2·1	2·532	2·8	2·854
1·0	4·613	2·2	2·832	3·0	3·137
1·05	4·795	2·4	3·636	3·2	3·457
1·1	7·672	2·6	4·925	3·6	4·257
1·15	11·11	2·8	7·328	4·0	5·364
1·2	19·46	3·0	13·40	4·8	9·736
1·25	69·39	3·2	59·70	5·6	31·49

Since in the example of the SiO_2 gel chosen the vapour pressure p_ω at O amounted to 0·84 cm. Hg (at O_1 0·57 cm.) and the saturation pressure at the temperature of 15° has a value of 1·27 cm. of Hg, we have from Table 169 for the widest capillaries a radius $r = 2{\cdot}746\ \mu\mu$, for the narrowest $r = 1{\cdot}376\ \mu\mu$. They are therefore actually of amicronic size, as required by the ultramicroscopic appearance (cf. p. 660). Upon the part of the curve from O_1—corresponding to 14 millimols H_2O to 1 gram SiO_2—to B the gel is again transparent and dry. Here we are doubtless dealing with a pure adsorption of water by silicic acid. That the curve does not end at the zero point, but at B, means that a residue of water (about 3 millimols per gram SiO_2) cannot be removed under the experimental conditions chosen, that is, not at ordinary temperature, but only upon heating. Perhaps this water is chemically combined, or the amount adsorbed only decreases at very much lower pressure ; in the latter case the curve from the origin through B to O_1 would quite correspond to the curve for wettable adsorbents as represented by Fig. 31, p. 164.

That this part of the curve refers to an adsorption is also confirmed by the entire reversibility of the hydration and dehydration. From point O_1 onwards this is no longer the case. During hydration the content of liquid corresponding to a given vapour pressure, is smaller than during

dehydration. This is probably due, according to Zsigmondy, to the capillary walls, which have become dry, being less easily wetted than during the removal of water. The meniscus in it is therefore less concave, the radius of curvature greater, the vapour pressure therefore also greater for the same content. The filling of the capillary spaces is correspondingly concluded at a point O_2 of higher vapour pressure. In agreement with the view that this hysteresis phenomenon is a matter of ease of wetting, is the fact that the amount of hysteresis, that is, the area OO_1O_2 included between the curves, is greater when we work in air, as van Bemmelen did, than in vacuo according to Zsigmondy. The displacement and dissolution of the air present upon the walls of the capillaries make the conditions for wetting still less favourable, the radius of curvature of the meniscus still greater.

From O_2 onwards along the stretch O_2C the saturation pressure is quickly reached with but little further absorption of water. The curve OA is not again reached. The gel is inelastic and does not again assume the highly swollen and water-laden state which holds along this part of the curve. If dehydration is again performed, the curve CO_2 is first passed over, which soon bends and runs into the curve OO_1. If the dehydration is interrupted at some point by renewed hydration, we get, as is easily intelligible, pieces of curve lying between the main curves. The curve AO is never passed over reversibly; if the drying is interrupted at a point D and hydration recommenced, we move along a curve DE, which corresponds to O_2C; the capillary spaces do not regain their original volumes. If on the other hand the gel is kept for a long time at the vapour pressure of the point D, the amount of absorbed water does not remain constant, but steadily declines; the gel walls lose their power of taking up water. The change which the silicic acid thereby suffers is probably only the continuation of that change which takes place from the start, even during the formation of the colloidal silicic acid in the sol, and expressed in the decrease in dialysability (cf. p. 626).

In favour of Zsigmondy's theory concerning the gain and loss of water by silicic acid gels we have the fact that with other liquids, such as alcohol and benzene, exactly the same phenomena are obtained, and at the points O and O_1 the same values for the capillary radii are calculated as for water. In Table 170 are the values so found from measurements by Anderson.[1]

TABLE 170

Capillary Radius of a SiO_2 Gel, calculated from the Saturation with various Liquids

$t = 15°$

Liquid.	p_ω (cm. Hg.).	r (in $\mu\mu$).
Calculation for upper opacity-point O		
Water	0·84	2·746
Alcohol	2·12	2·587
Benzene	2·9	2·990
Calculation for lower opacity-point O_1		
Water	0·57	1·376
Alcohol	1·3	1·212
Benzene	1·2	1·351

[1] *loc. cit.* p. 663.

The velocity of absorption of liquid also agrees well with the theory. The first amount of liquid up to point O_1 is taken up quickly ; this corresponds to the rapid adsorption velocity (cf. p. 107). If the amount taken up increases, so as to lie between O_1 and O_2, the absorption takes place much more slowly, but very uniformly, with almost constant velocity ; the filling of the capillaries is taking place under uniform conditions. The equilibrium near the saturation pressure is finally reached very slowly and asymptotically ; we are dealing with a sorption in the micellæ of the gel.

It has already been remarked, that when the opacity-point is reached as the gel dries, the latter usually commences to become turbid in the interior. The fine air or gas bubbles are formed there, and not at the external surface where the evaporation takes place. This at first appears surprising, but becomes intelligible when we consider that with capillaries of 2·5 to 4 $\mu\mu$ radius water has a capillary rise of from 5 to 10 kilometres. The liquid inside hence stands under strong tension. Liquid evaporating outside is immediately replaced from the interior, and the liquid is torn, as in the experiments discussed earlier (p. 10), at the point of least resistance ; that is, especially at places where air or gas is already present. Zsigmondy's theory assumes all through that the adsorption layer is generally considerably thinner than the still very fine capillaries ; it agrees more with Langmuir's (p. 130) than with Polanyi's view (p. 123).

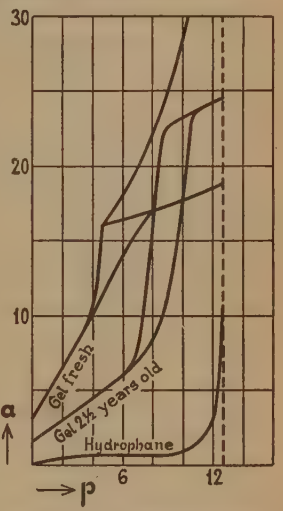


Fig. 127.—Vapour-pressure Isothermals of SiO_2 Gels of various Ages.

During ageing of the gel, the micellæ and the intervening capillary spaces become continually coarser ; hence the vapour pressure between the opacity-points OO_1 continuously approaches the saturation pressure. If the radius of the capillary spaces increases to more than 20 to 30 $\mu\mu$, the vapour pressure in the opacity-region is not sensibly different from that of the saturation pressure, and we have a vapour-pressure curve such as is reproduced in Fig. 31 as adsorption isothermal for wettable adsorbents. In Fig. 127 the vapour-pressure curves for SiO_2 gels of various ages are shown. As the limiting curve of a greatly aged gel with coarse capillary spaces, that of the mineral hydrophane is given ; in this the radius of the capillaries therefore exceeds the limit at which the latter fill up at a sensibly lower pressure than the saturation pressure.

Heating the SiO_2 gel has not exactly the same effect as natural ageing.[1] Apparently the electrolyte content thereby plays a part, since salt-free gels sinter much less when heated than those containing salts. The opacity-point obtained by dehydrating the heated gel is not displaced to a considerable extent with regard to the unheated. But the whole region of hysteresis is much smaller. Apparently the diameter of the capillaries still present has remained sensibly the same. But the total volume of the capillary spaces has become smaller, doubtless because many capillaries have collapsed completely, and the vapour is thus prevented from entering at many points of the gel.

[1] *Zsigmondy*, Zeitschr. f. anorg. Chemie, **71**, 372 (1911).

Similar vapour-pressure isothermals were found by van Bemmelen for silicic acid gels and also for those of copper and iron oxide. The behaviour of cocoanut charcoal may also be interpreted in this way. Bachmann [2] found in it two hysteresis regions, as if two kinds of capillary cavities were present; coarser ones of about 10–40 $\mu\mu$ diameter, and finer ones of 5–6 $\mu\mu$. With this charcoal the following fact was also remarkable. If the ignited and water-free charcoal was saturated with water vapour and then dehydrated again, drying over sulphuric acid did not restore the original state of complete dryness. About 8 per cent. of water remained bound, probably dissolved in the micellæ. Permutite has, according to Bachmann,[3] coarse capillaries, similar to hydrophane.

What distinguishes the non-elastic gels and causes their technical application is the fact that they suck up any liquid, and that the liquid distributed in the capillary skeleton can be handled with much less danger. If the liquid, for instance, is explosive, a local decomposition can attain the nature of an explosion with much greater difficulty by adiabatic heating since the extended walls of the micellæ present everywhere take up much heat and produce great cooling. Another advantage with liquids taken up in gels is that by the adsorption and lowering of vapour pressure in capillary spaces the vapour pressure of strong-smelling or corrosive liquids is diminished, and they may be applied more conveniently. Examples of this application of inelastic gels are dynamite and the "solid bromine" used for disinfection purposes; kieselguhr serves as inelastic gel, nitroglycerine and bromine respectively are the liquids.

Absorption and Loss of Liquid by Elastic Gels

In the case of elastic gels the gain and loss of liquid proceeds very differently. No opacity-point is observed on drying. The gel remains essentially unaltered in appearance, and hence transparent, if originally so, and decreases uniformly in volume until, as in the case of gelatine for instance, it dries up to a horn-like solid. The absorption of liquid likewise proceeds with a steady increase in volume, without the appearance of an opacity point. The absorption of liquids by elastic gels, which proceeds with increase of volume, will be described as *swelling* (*Quellung*). Many workers employ the term *Quellung* to denote the taking-up of water by all gels, including the inelastic ones. Although there is no fundamental objection to this, it appears to me that the idea of *Quellung* is so closely connected with that of an increase of volume, that I prefer to use the word in the old concrete sense. The loss of liquid by elastic gels is accompanied by *shrinkage* (*Entquellung*).

The final state of swelling towards which the gel tends, depends upon the nature of the gel and the liquid. Many gels swell in many liquids only to a limited extent. A definite, large amount of liquid is imbibed by the gel, while only a small or undetectable amount of gel is peptized by the liquid. Such limited swelling is found, for instance, in the case of agar, many proteins such as globulin, fibrin, etc., in pure water, caoutchouc in organic liquids such as benzene, chloroform and others. The swelling of gelatine in water is usually regarded as limited in extent; according to Arisz [5] it is questionable whether this is correct. It is completely pep-

[1] *loc. cit.* p. 663.
[2] Zeitschr. f. anorg. u. allgem. Chemie, **100**, 32 *et seq.* (1917).
[3] Zeitschr. f. anorg. u. allgem. Chemie, **100**, 38 *et seq.* (1917).
[4] *Marcus*, Verh. deutsch. Naturf. u. Ärzte, 1911, II, second half, pp. 465 to 466.
[5] Kolloidchem. Beihefte **7**, 48 *et seq.* (1915).

zed in pure water at 30°, and at lower temperatures apparently no real uilibrium is reached, but the imbibition of water proceeds continuously, though very slowly ; below 10° it is, however, practically inappreciable. erhaps the tendency to peptization is not yet so decided that it completely asks the tendency to attain a limited state of swelling. Other gels on .e contrary imbibe liquids without limit ; they swell as the liquid pene- ates into them, but finally become completely peptized, as has already en mentioned regarding the albumins, gum arabic, peptones, and so on. ne cannot simply say without reference to the dispersion medium that ith one gel the swelling is limited and with another unlimited. The velling of gelatines in pure water, for instance, may be regarded as limited ; a low temperature ; but gelatines are fully peptized by a fairly con- ntrated aqueous potassium thiocyanate solution (1 to 2 molar), in which, nerefore, they swell without limit.

A further important difference between astic and non-elastic gels consists in the fol- wing. Non-elastic gels take up any liquid hatever, provided it wets the gel ; hence with iO_2 gels the vapour-pressure isothermal could e determined with such different liquids as ater, alcohol, and benzene (p. 666). Elastic els, however, cannot imbibe every liquid. elatine, proteins and so on swell in water, queous solutions, and glycerine, but not in lcohol, benzene and the like ; viscose and archment paper swell appreciably only in ater,[1] not in alcohol, methyl alcohol, or other rganic liquids ; pig's bladder much the most trongly in water, but also quite considerably n methyl alcohol, glacial acetic acid, and methyl cetate, and much more weakly in other al- ohols and esters, chloroform, ether, benzene nd the like[2] ; caoutchouc on the contrary ery strongly in the hydrocarbons and their alogen compounds (benzene, xylene, chloro- orm, carbon disulphide and others), and progressively less in ethyl acetate, cetone, acetic acid, alcohol, and water.[3] Acetyl cellulose swells slightly n pure water and pure alcohol, but strongly in mixtures of the two.[4]

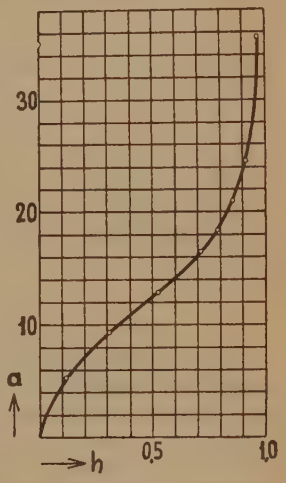


Fig. 128.—Vapour-pressure Isothermal of Gelatine Gel.

Katz[5] determined the vapour-pressure isothermals of a large number f gels such as gelatine, agar, proteins (ovalbumin, fibrin, spongin, casein nd others), nuclein, gum arabic, and dextrin, which swell to a limited or nlimited extent in water, over their whole range. He used for the purpose an Bemmelen's method (p. 663) of allowing equilibrium to be set up in lesiccators containing sulphuric acid solutions of various concentrations n the presence of air ; by working in vacuo he obtained less definite results. The vapour-pressure isothermals show throughout the form reproduced in Fig. 128 for gelatine, which was discussed on p. 163 as general adsorption.

[1] *Flusin*, Ann. d. chim. et d. phys. (8), **13**, 480 (1908).
[2] *Flusin, loc. cit.*
[3] *Flusin, loc. cit.*
[4] *Knoevenagel*, Kolloidchem. Beihefte **13**, 193 (1920).
[5] *loc. cit.* p. 659. In this very penetrating investigation a comprehensive considera- tion of the literature will be found.

isothermal for wetting liquids, and which holds in limiting cases for coarse capillary cavities and also for the taking-up of liquid by non-elastic gels (p. 667); in Fig. 128 the amounts adsorbed in millimols are plotted as ordinates, the relative vapour pressures as abscissæ. In Table 171 the amount a of water taken up (in grams and in millimols) per gram of dry gel is given together with the relative vapour pressure h.

TABLE 171

Vapour-pressure Isothermal for Swelling of Gelatine in Water Vapour
Room Temperature

h (Relative Vapour Pressure).	a (Amount of Water taken up per gram of Dry Gelatine in	
	Grams.	Millimols.
0	0	0
0·020	0·033	1·83
0·122	0·095	5·27
0·306	0·168	9·32
0·525	0·232	12·9
0·718	0·298	16·5
0·793	0·328	18·2
0·857	0·376	20·9
0·915	0·442	24·5
0·965	0·641	35·6
1·000	4·6	255

Katz was able to show in particular that the initial part at low pressures corresponds to the ordinary adsorption isothermal, which then bends round at higher pressures to an adsorption saturation (see p. 163). The points of the curve may be reached reversibly from above and below, sometimes, it is true, only after weeks or months. With many gels (such as gelatine and agar) the fresh product shows hysteresis phenomena, which become insignificant, however, after a few days (cf. p. 718).

There is no objection from previous considerations to the interpretation of this taking-up of liquid by a swelling gel as an adsorption. With non-swelling gels, such as SiO_2, the micellæ experience irreversible changes, by which they become progressively more rigid and less hydrophilic; hence upon drying a limit can be reached at which they are too rigid to close up further, and hence leave capillary spaces open as described in the previous section. Upon being again brought into contact with water they only take it up in so far as they fill their capillary spaces, without the micellæ, which have become coarser and more rigid, being again subdivided and the gel softened anew. In the case of swelling gels, on the other hand, the micellæ do not lose their power of again taking up liquid reversibly. They do not become so rigid, but remain flexible enough to pack as closely as possible together, whereby they retain their individuality, and do not become sensibly coarser. In the dried gel the micellæ will be very closely associated with one another, but nevertheless not so closely as the molecules in a glass, which appears completely homogeneous in the ultra-microscope, and has been formed from a homogeneous melt. If now the imbibed liquid acts on the dry gel, the single micellæ take up, for instance, water molecules—perhaps even become hydrated in the true sense—enlarge their

volume, and finally reach the end state of limited swelling when each micella has saturated itself with water molecules in accordance with its adsorptive power. This will be effected by liquids the molecules of which have a sufficiently strong affinity for the micellæ ; water and aqueous solutions with hydrophilic substances such as gelatine, albumin, and so on, organic liquids with hydrophobic substances such as caoutchouc. The difference as compared with the taking-up of water say by glass is due to the structure of the latter being too narrow and rigid, so that the water is only adsorbed on the surface and does not penetrate (or only very slowly) into the interior, while the structure of the swelling gel is simply much looser and allows adsorption at all internal surfaces. With inelastic gels the inner walls behave like glass ; but it is the capillaries which, as described above, fill themselves with water ; they are, it is true, amicronic, but still wider as compared with the capillaries contained in a dry elastic gel. A sharp distinction between true imbibition and adsorption of vapour at a free surface of the solid substance is not, however, advisable. A certain boundary will exist in so far as swelling presupposes a stronger attraction between the micellæ and the liquid than between the micellæ themselves.

Katz on the other hand upholds the view that the swelling of a gel is to be regarded as the formation of a solid solution of the imbibed liquid in the gel. If we consider the effective forces, the difference in the two views is not essential, for with solution molecules which, according to Katz, are formed, as with adsorption, it is a matter of the saturation of residual valencies. Katz emphasizes strongly the monophasic nature of the dry and swollen gels. What may be said against this was put forward above (p. 659). The objections raised by Katz[1] to the results of ultramicroscopic investigations I regard as entirely unfounded.

It is further possible to transform elastic into inelastic gels, and to demonstrate in the latter the opacity-point and the absorption of very different liquids in the capillary skeleton ; this is a convincing indication of a heterogeneous structure. This succeeds, for example, with gelatine gels, by bringing the gels into water-alcohol mixtures of increasing alcohol content, leaving them sufficiently long therein, and so finally displacing the water as completely as possible by more and more concentrated alcohol.[2] This gelatine gel treated with alcohol and which no longer swells shows, according to Bachmann, precisely the same phenomena of opacity-point and so on as a silicic acid gel, and not only with alcohol, but also with other liquids such as benzene.

That liquids such as sulphuric acid and phosphoric acid bind water very firmly in small amounts, while with increasing water content the vapour pressure of pure water is approached, and hence have vapour-pressure curves of similar form to gels,[3] is entirely intelligible, but tells in no way against the polyphasic structure of gels.

At the point where the vapour-pressure curve rises so steeply in the neighbourhood of the saturation pressure (see Fig. 128, p. 669) the amount of liquid taken up by the gel alters very greatly with minute changes in the vapour pressure. This has the result, in the first place, that the points on this part of the curve are difficult to determine ; and further, that, if

[1] Kolloidchem. Beihefte **9**, 14 (1917).

[2] *Bütschli*, " Ueber den Bau quellbarer Körper und die Bedingungen der Quellung," Gottingen, 1896. *Bachmann*, Zeitschr. f. anorg. u. allgem. Chemie, **100**, 1 (1917).

[3] *Katz*, Kolloidchem. Beihefte **9**, 118 *et seq.* (1917).

the greatest care is not taken to have equality of vapour pressure, apparently equal pressures correspond to very different amounts of liquid in the swollen gel. Hence it is difficult to determine the so-called *maximum swelling*, that is, the amount of liquid taken up by gels with a swelling limit at the saturation pressure of the pure liquid. Hence also a comparatively large amount of water may be removed from a moist gel without the vapour pressure sensibly falling. Nernst [1] points out that if, for example, peat be dried by electrosmosis (cf. p. 273), the side at which the water leaves has a vapour pressure only slightly less than that of the other side, and that therefore the efficiency of the drying is not great.

The so-called Schroeder's [2] paradox, which has frequently been discussed,[3] depends upon this circumstance. P. v. Schroeder had observed that a gel which had become very swollen in water, when brought at the same temperature into the vapour space over this water, lost water. It thus appeared as if the equilibrium attained in the liquid was not maintained when the gel was placed in the vapour space over this liquid. L. K. Wolff and Büchner [4] showed that in large glass desiccators, with which v. Schroeder worked, there is no guarantee that the vapour pressure is strictly constant in the whole gas space. Small changes on account of slight temperature variations do not equalize themselves so rapidly as is frequently assumed. Hence the differences observed by v. Schroeder become slight when small desiccators are used. They disappear when water and gelatine are enclosed in a metallic capsule, itself contained in a larger desiccator, or if air carefully saturated with water vapour at the same temperature is led over the swollen gelatine. Katz [5] points out that the physicists at the commencement of the nineteenth century, who investigated the behaviour of the hygrometer in detail, already knew how difficult it is to maintain the vapour pressure of water in a space as constant as is required for gels at their maximum swelling. Thus Deluc [6] had already observed the Schroeder paradox, on strips of whalebone, which he used for such measurements. Only when he put them into a case of metal wire, over which cloth was stretched, and allowed water to drop on the cloth, so that the gel was surrounded on all sides by evaporating water, did the strips of whalebone behave in the vapour as in liquid water.

Hysteresis phenomena, processes which take place more quickly with liquid water than with vapour, are probably also partly responsible for this paradox, which point will be discussed later (p. 710).

The Swelling Pressure

The absorption of liquid during the swelling of a dry gel causes a sensible increase in volume of the gel; if this increase in volume meets with resistance, it is capable of exerting a considerable pressure. A counter-pressure may be applied which just prevents further increase in volume. This is the *swelling pressure*, which is in equilibrium with a definite liquid content

[1] Ber. d. deutsch. physik. Ges. **11**, 112 (1909).
[2] Zeitschr. f. physik. Chemie, **45**, 109 *et seq.* (1903).
[3] E.g. *Bancroft*, Journ. Phys. Chem. **16**, 395 (1912); *L. K. Wolff* and *Büchner*, Koninkl. Akad. v. Wetensch. Amsterdam, **15**, 1078 (1913); **17**, 92 (1914); Zeitschr. f. physik. Chemie, **89**, 271 (1915).
[4] Zeitschr. f. physik. Chemie, **89**, 271 (1915); Koninkl. Akad. v. Wetensch. Amsterdam, **17**, 92 (1915).
[5] Kolloidchem. Beihefte **9**, 48 *et seq.* (1917).
[6] Phil. Trans. **81**, 1, 389 (1791).

of the gel. A corresponding pressure must be exerted in order to press liquid out of a gel. It may already be remarked here, as will be discussed more in detail later (p. 714), that swelling is accompanied by a nett decrease in volume, that is, the sum of the original volumes of the dry gel and of the liquid is greater than the volume of the swollen gel.

The swelling pressure may take on very high values. Experiments are known in which peas filling a skull are able on imbibing water to force its bones apart, or in which wood swollen by water bursts rocks apart.[1] This fact is the reason, although not the sole one, why the swelling pressure is not easy to measure and why it is not known with the accuracy its importance demands. Reinke [2] was the first to measure swelling pressures, the substance used being discs of a sea-alga *Laminaria* in water. He termed the apparatus which he employed an œdometer ; it was constructed as follows. The laminaria disc was placed in a hollow metal cylinder ; upon it rested a metallic piston with many small holes in it, through which the liquid entered from above. The piston carried above a disc which could be loaded with weights. A pointer allowed the small amount by which the piston was raised during swelling to be determined. The œdometer easily fails with gels such as gelatine and caoutchouc, which become so soft during swelling that they are pressed through the holes in the piston.

An apparatus designed by E. Posnjak [3] is somewhat more widely applicable and convenient (Fig. 129).

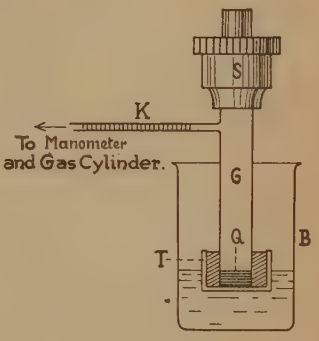


Fig. 129.

A glass tube G carries a porous earthenware cylinder T cemented to it at the bottom. The disc of the swelling gel is placed at Q at the bottom of the tube ; this is otherwise completely filled with mercury, which is continued into the calibrated capillary K. G is carefully closed above by a screw-piece S ; below, the clay cylinder dips into a beaker B filled with the liquid. The capillary is connected at its end with a gas-bomb, which allows pressures up to 6 atmospheres to be exerted on the mercury and the swelling disc. From the level of the mercury in the capillary tube the volume change of the gel may be determined, and therefrom the amount of liquid imbibed.

E. Posnjak determined with this arrangement the swelling pressure of raw caoutchouc in many organic liquids and of gelatine in pure water.

The pressures were set up readily and reversibly in the course of a few days. The swelling pressure decreases greatly with increase in the liquid content of the gel, and hence increases with increasing disperse phase content. It is for various reasons useful to refer the swelling pressure P, not to the amount a of liquid taken up by the gel, but to the concentration

[1] Concerning an application of swelling pressure in ancient Egypt see *Katz*, Kolloidchem. Beihefte **9**, 30 (1917). I owe to Dr. *Jaenicke* the information that this method was quite general in antiquity ; cf. *Blümner*, "Technologie und Terminologie der Gewerbe und Künste bei Griechen und Römern," 1884, 3 vols, pp. 78–79. [This practice is also quite general at the present day in quarrying jointed rocks. The "taking-up" of a wooden vessel is another common instance. Wearable parts of machinery, such as rolls and stamps, are also fixed in place in this way, a necessary condition being that the wood used must always remain wet.—(*Trans.*)]

[2] Hanstein's Botan. Abhandl. **4**, 1 (1879).

[3] Kolloidchem. Beihefte **3**, 417 (1912).

c of the disperse phase. The concentration c (grams of dry gel per 1,000 c.c. gel + liquid) is connected with a by the relation

$$c = \frac{1{,}000}{V_G + aV_F} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where V_G and V_F are the specific volumes of gel and liquid. The decrease in total volume taking place during swelling is not taken into account thereby. The relation between P and c may be to a large extent represented by a formula

$$P = P_0 c^k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which P_0 and k are constants. Tables 172 and 173 show to what extent it is fulfilled.

TABLE 172[1]

Swelling of Gelatine in Water

Weight of the gelatine disc used, 0·0600 g.
Room temperature. $P_0 = 0{\cdot}00002704$; $k = 2{\cdot}9715$

P (in grams per sq. cm.).	c (obs.).	c (calc.).
520	306·3	283
720	317·1	315
1,120	361·3	366
2,120	460·5	454
3,120	504·4	517
4,120	555·0	567
5,120	613·3	610

TABLE 173[1]

Swelling of Raw Caoutchouc in Benzene

Weight of caoutchouc disc, 0·0667 g.
Room temperature. $P_0 = 0{\cdot}0007885$; $k = 2{\cdot}77$

P (in grams per sq. cm.).	c (obs.)	c (calc.).
720	144·6	144
1,120	164·2	166
2,120	208·1	209
3,120	240·0	241
5,120	289·4	288

The experiments of Reinke on *Laminaria* obey this formula. The exponent k is, according to available data, only little dependent upon the nature of the gel and the liquid, and has a mean value of about 3 (cf. Table 174). If we wish to bring P in relation to a, it follows from equations (1) and (2), if we put $V_F = 1$ (for water),

$$P = P_0\left(\frac{1{,}000}{V_G + a}\right)^k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

[1] Recalculated from *Posnjak's* measurements.

The maximum swelling (see p. 672) is naturally likewise a point on the P, a curve; it is that amount a of liquid which is taken up by the gel when only the pressure of the liquid vapour or only atmospheric pressure bears on the gel, according as we work in vacuo or in air. The value of the maximum swelling has been more frequently measured than the complete swelling-pressure curve.

TABLE 174

Swelling Exponent k for various Gels and Liquids

Room temperature

Gel.	Liquid.	k.
Gelatine	Water	2·97
Laminaria	„	4·13
Raw caoutchouc	Benzene	2·77
„	Toluene	2·56
„	Cymene	2·48
„	Ethyl ether	3·01
„	Chloroform	2·64
„	Carbon tetrachloride	2·53
„	Ethylene chloride	3·33
„	Tetrachlorethane	2·86
„	Acetylene dichloride	2·48
„	Thiophene	2·98

It may be comparatively simply measured as follows.[1] The dry gel is dipped into the liquid to be imbibed; then taken out from time to time, wiped with filter paper in order to remove the excess of liquid adhering to it, and weighed. The maximum swelling is reached when the weight no longer alters. Usually the gel is so soft in the neighbourhood of maximum swelling that the determinations become very inexact. The value of the maximum is therefore also obtained by extrapolation from the curve of increase of weight with time.

The dependence of the maximum swelling, or more generally of the amount of liquid taken up at any pressure upon the nature of the liquid, has only been examined in detail in the case of caoutchouc, which imbibes a large number of organic liquids. Simple regularities are not to be recognized in Table 175, which relates in particular to the swelling of raw caoutchouc; they are, indeed, also unknown as regards the adsorbability of the substance. Very striking is the strong imbibition of compounds containing halogens, such as carbon tetrachloride and chloroform. Flusin's measurements [2] of the maximum swelling by vulcanized rubber run largely parallel to these, which were made on raw caoutchouc and at an excess pressure of 1,120 g. per sq. cm.

In the case of swelling pressure we are dealing with definite equilibria, and hence thermodynamic conclusions may be drawn without hesitation. First we get a relation between swelling pressure and vapour pressure of

[1] *Hofmeister*, Arch. f. exper. Pathol. u. Pharmakol. **28**, 210 (1891); *Spiro*, Beitr. z. chem. Physiol. u. Path. **5**, 276 (1904); *Wo. Ostwald*, Pflüg. Archiv, **108**, 563 (1905); **11**, 581 (1906).

[2] *loc. cit.* p. 669.

TABLE 175

Dependence of Swelling on the Nature of the Liquid

Room Temperature

Liquid.	Amount of Liquid taken up (millimol per gram. of Raw Caoutchouc) at an excess Pressure of 1,120 g. per sq. cm.	Amount of Liquid taken up (millimol per gram of Vulcanized Caoutchouc) without excess Pressure from Flusin's Experiments.
Benzene	56·5	66·2
Toluene	50·5	69·5
Cumene	34·4	—
Cymene	32·7	—
Ethyl ether	32·4	33·2
Chloroform	78	120
Carbon tetrachloride	71·9	—
Ethylene chloride	27·3	—
Acetylene chloride	75·9	—
Thiophene	63·3	—

a gel.[1] Two gels, 1 and 2, completely similar as regards composition and structure, are assumed to be swollen to different degrees, the one standing under a swelling pressure P_1, the other under P_2. If the volume dV of liquid be pressed out of 1, and allowed to enter 2, then the work

$$(P_2 - P_1)dV$$

is gained. The isothermal cycle is closed by allowing the amount dw of liquid corresponding to volume dV, to distil back from gel 2 at the vapour pressure p_2 to gel 1 at the vapour pressure p_1. The work is

$$\frac{RT}{M} \log \frac{p_1}{p_2} dw.$$

If the sum of the work is equated to zero, then

$$\frac{1}{P_2 - P_1} \log \frac{p_1}{p_2} = -\frac{M}{RT} \frac{dV}{dw} = -\frac{MV_0}{RT} \quad . \quad . \quad . \quad . \quad (4)$$

since $\frac{dV}{dw}$ is equal to the specific volume of the liquid V_0. Since the expression $\frac{MV_0}{RT}$ is always positive, it follows from equation (4) that, if $P_2 > P_1$, then necessarily $p_2 < p_1$, and vice-versa; *the gel which stands under the larger swelling pressure has the lower vapour pressure.*

If we introduce

$$P_2 = P_1 + dP_1 = P + dP$$

and

$$p_2 = p_1 - dp_1 = p - dp$$

we get finally

$$\frac{1}{p} \frac{dp}{dP} = -\frac{MV_0}{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$P = -\frac{RT}{MV_0} \log p + \text{Const.}$$

[1] *Freundlich* and *E. Posnjak*, Kolloidchem. Beihefte **3**, 443 *et seq.* (1912).

At the saturation pressure p_s, $P = 0$, hence

$$P = -\frac{RT}{MV_0} \log \frac{p}{p_s} = -\frac{RT}{MV_0} \log h \quad . \quad . \quad . \quad . \quad . \quad (6)^1$$

—a relation first obtained by Katz.[2]

On the basis of these equations the swelling pressure of a gel may be calculated from the relative vapour pressure h. If this is done for the numerous cases measured by Katz, it appears that a comparison with the values directly measured can only be made with caution. The vapour pressures determined by Katz lie much lower, the swelling pressures obtained from them therefore higher than those measured directly. Thus the highest swelling pressure measured for gelatine, about 6,000 g. per sq. cm., corresponds to a vapour pressure of 0·995, while the highest relative vapour pressure measured by Katz for gelatine amounts to 0·965. Nevertheless, the swelling pressures which can be calculated for gelatine from the highest vapour pressures measured by Katz, connect up quite satisfactorily with the measured values of Table 172, in so far as they likewise obey formula (2), with an exponent k of about 5. Also, the swelling pressures calculated by equation (2) from the vapour pressure measured by Katz at the lowest concentrations agree in order of magnitude with the observed ones, and more is not to be expected, since the gelatine preparations were quite different. At the higher swelling pressures, as may be deduced from Katz's measurements, P increases with increase in c more rapidly than required by equation (2), apparently taking a similar course, but with a higher exponent.

From the Katz vapour-pressure measurements may be calculated the very large swelling pressures which it has not been found possible to measure directly. Thus we have from Table 171 already for $a = 1{\cdot}83$ millimol per gram gelatine and a relative vapour pressure of 0·020, a swelling pressure of about 5,000 atmospheres.

Equation (6) agrees largely with the equation

$$P = -\frac{RT}{MV_0} \log \frac{p_L}{p_M}$$

in which P is the osmotic pressure, p_M the vapour pressure of the pure solvent, p_L that of the solution, M and V_0 molecular weight and specific volume of the solvent. The swelling pressure thus plays a similar part in swelling phenomena to that played by the osmotic pressure in osmotic phenomena.[3]

This is true with a very noteworthy limitation. For the osmotic pressure we have

$$P = RTc.$$

It is proportional to the molar concentration. In this is contained the fact that it is of kinetic nature, and that the impacts of the dissolved molecules on the semi-permeable wall take place independently of one another. The formula holding for the swelling pressure

$$P = P_0 c^k$$

expresses, as will later appear more clearly (p. 683), the fact that it is not

[1] In all these considerations the diminution in total volume during swelling is neglected.

[2] Kolloidchem. Beihefte **9**, 106 (1918).

[3] *Freundlich* and *E. Posnjak*, Kolloidchem. Beihefte **3**, 445 (1912).

the expression of a kinetic, but of a potential energy. In the different nature of the dependence upon c the fact is revealed that the micellæ of the gel are not independent of one another, but that the dependence of the swelling pressure upon the micella concentration at large and small liquid content remains of a like nature, for equation (2) gives when differentiated

$$\frac{dP}{P} = k\frac{dc}{c};$$

the ratio of the relative change in swelling pressure to relative change in concentration is constant.

Just as the osmotic pressure allows constructions to be made by means of which chemical energy may be transformed into mechanical energy, so also does the swelling pressure, in accordance with the resemblance just discussed; for one may probably regard the loose affinity of adsorption as chemical energy. In living beings, Nature makes extensive use of this possibility of transformation by means of the swelling pressure.

It was already mentioned on p. 552 that Wo. Ostwald would like to regard quite different phenomena as due to swelling pressure. He assumes that in concentrated solutions of strongly hydrophilic substances the osmotic pressure measured is not alone the true kinetic osmotic pressure, but that the static swelling pressure is also included in it. The solution molecules have not yet saturated themselves with water and strive to take up more from the external liquid, whereby the pressure is increased. How far this view is confirmed by the osmotic phenomena of sols was discussed earlier (p. 552). Here we will only add that in concentrated aqueous sugar solutions the directly measured osmotic pressure increases far more rapidly than in proportion to the concentration, and that Wo. Ostwald was able to calculate the observed P, c curve—dependence of observed osmotic pressure upon concentration—from formula (3), p. 552; this pressure proves to be the sum of the kinetic osmotic pressure and the swelling pressure. The exponent k also had the same value of 2 to 3 as in the case of the swelling pressure.

Some Mechanical Effects of Swelling and Shrinkage

Some mechanical consequences of swelling were alluded to in the previous section. The variety of such effects is very great, and it may be foreseen that a wide range of investigations will open out when the questions are raised: what form does a gel take upon swelling if it has a given form or if it has different swelling capacities in different parts? And: what motors may be constructed with swelling gels? The answers to these questions are important, if we wish to be able to say something concerning the many forms and structures and mechanical arrangements and muscular motors occurring in living beings. Though it is necessary to be very careful in these matters in passing from laboratory experience to natural structures, it cannot on the other hand be doubted that swelling plays a decisive part in these structures. Science has only just commenced to deal with these questions, so that here attention can only be drawn to a few facts.

If a rectangular piece of a gel, for instance, a gelatine gel, be allowed to imbibe water, it becomes somewhat longer and above all thicker. In apparent contradiction with this is the fact that thread-like structures, like catgut, frequently become shorter and not longer on swelling. This

depends, as Bernstein [1] has shown, upon the fact that the threads and strings consist of several spirally wound threads. When these become thicker on swelling, the result is that they attempt to move away from the common central axis; since their length remains practically unaltered, the thread must become shorter as a whole. Bernstein wishes to conclude from this that the Engelmann swelling theory of muscular contraction,[2] which made the muscle equivalent to a swelling piece of catgut, cannot be upheld, since muscles do not show a spiral structure microscopically. This conclusion is perhaps not valid, for radiographically a still finer structure of the muscles may be established,[3] and this possibly depends on a spiral structure of the finest threads which are the actual building stones of the muscles. In any case we cannot yet say with certainty what part swelling and shrinkage phenomena have in the process of muscular contraction.[4] There, as in other cases, swelling phenomena of a rapid and violent character appear to occur, such as have not yet been realized in the laboratory. We may draw attention here to the spring mechanism of the cardoblast of cœlenterata, in which, according to Will,[5] a thread of gel, coiled spirally against the nematocyst wall, is suddenly allowed to swell, whereby the nematocyst is turned inside out explosively (as it were), and is able to burst through thick layers of secreted chitin.

Spek [6] investigated the foldings which occur when a plate of gel consisting of two firmly adhering plates of different swelling capacities is allowed to swell. For special reasons he did not use plates, but spherical surfaces, which consisted of a complete spherical surface of a weakly swelling gel and an inner spherical surface which only covered a calotte of the inner wall and was made of a more strongly swelling gel. A mixture of gelatine and agar (20 per cent. gelatine + 3 per cent. agar, in the ratio 1 : 3) served for the more weakly swelling gel, and gelatine for the more strongly swelling gel. The layer of the latter now strives to occupy the larger surface, and hence to assume a convex curvature instead of the concave; the part of the spherical surface which is coated inside with pure gelatine is thereby dented inwards. These experiments were suggested by an idea of Bütschli's [7] that the indentation in gastrula-invagination might be brought about in this way, and in actual fact the likeness of the resulting forms with those in the latter phenomenon is very great. How Spek has also tried to explain other biologically important foldings and curvings in this manner, and how he interprets the rôle of the different ions in the development of sea-urchin larvæ from the point of view of their favourable or unfavourable influence on swelling, cannot here be dealt with in detail.

A strong mechanical effect of shrinkage may be observed when gelatine layers are allowed to dry upon glass. The gelatine sticks so strongly to the glass, and the force with which it shrinks is so great, that the glass plate is fractured, or splinters are torn from its surface.[8] If glass plate and gelatine layer are chosen of suitable thickness, it may be arranged that the

[1] Pflüg. Archiv, **162**, 1 (1915).
[2] "Über den Ursprung der Muskelkraft," 2nd Ed., Leipzig, 1893.
[3] *R. O. Herzog* and *W. Jancke*, "Festschrift der Kaiser Wilhelm-Ges.," 1921, p. 118.
[4] See among others *O. v. Fürth*, Ergebn. d. Physiol. **17**, 363 (1919); *Meyerhof*, Pflüg. Archiv, **182**, 232, 284 (1920).
[5] "Die Klebkapseln der Aktinien und der Mechanismus ihrer Entladung," Rostock, 1909. Abh. d. Kgl. Preuss. Akad. d. Wiss. Phys-math. Kl. Nr. 1 (1914).
[6] Kolloidchem. Beihefte **9**, 259 (1918).
[7] Sitzungsber. d. Heidelb. Akad. d. Wiss., 2 Abh., 1915.
[8] See e.g. *Cailletet*, Compt. rend. **134**, 400 (1902).

glass is only bent, an arrangement more suited to a measurement of the force.

The force with which gelatine sticks to glass is also the essential cause of the curious effect that upon freezing a thin layer of gelatine spread upon glass, after evaporation of the ice the gelatine layer remaining behind reproduces the ice-crystals in relief. According to Liesegang [1] it is a matter of the following chain of processes. With slow freezing not too far below the freezing-point ice is formed outside the gelatine gel, the growth of the crystals removes water from the gel. This proceeds in one particular direction until the shrinking gel, owing to its firm attachment to glass, blocks the further growth of the ice crystal in this direction. It then grows further in another direction in which it does not find this resistance. The tensions occurring during shrinkage on the one hand, and certain directions of dehydration conditioned by the structure of the crystal and the velocity of crystallization on the other, produce structures in relief similar to the ice-flowers.

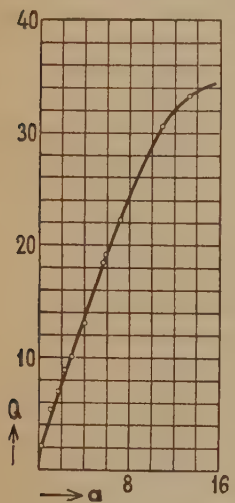


Fig. 130.—Dependence of the Heat of Swelling upon the Water Content with a Gelatine Gel.

The Heat of Swelling

Heat is quite generally developed during swelling. The amount of heat thereby produced is so great that it cannot escape direct observation. Hence the heat of swelling has long been known, quantitative measurements were carried out especially by Wiedemann and Lüdeking,[2] and very careful ones on starch and wood-fibre by Rodewald and his co-workers,[3] and then by Rosenbohm [4] on gelatine and agar, and by Katz [5] on casein, nuclein, and other substances. The measurement may be carried out by known thermochemical methods.

The *total heat of swelling* is—like the total heat of adsorption—determined as that amount of heat in g.-calories which is developed when 1 g. of dry gel takes up a grams of liquid. It is obtained as a difference between two amounts of heat, the heat of swelling Q_1 of the completely dry gel, and Q_2 that of the partly swollen gel, which has therefore adsorbed, over water and sulphuric acid, for instance, an amount a of liquid per gram of gel. As Fig. 130 shows, the total heat of swelling increases as a increases, but the increase is smaller, the larger a becomes. According to Katz it may be satisfactorily represented by an equation

$$Q = Q_1 - Q_2 = \frac{\alpha a}{\beta + a} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which α and β are constants (see Table 176).

[1] Particularly Kolloidzeitschr. **10,** 225 (1912); Prometheus, **25,** 369 (1914).

[2] *loc. cit.* p. 627.

[3] *Rodewald,* Landwirtsch. Versuchsstat, **45,** 201 (1894); *Rodewald,* "Untersuchungen über die Quellung der Stärke," Kiel and Leipzig, 1896; *Rodewald,* Zeitschr. f. physik. Chemie, **24,** 193 (1897); **33,** 593 (1900); *Rodewald* and *Kattein, ibid.* **33,** 579 (1900); *Volbehr,* "Die Quellung der Holzfaser," Diss., Kiel, 1896.

[4] Kolloidchem. Beihefte **6,** 177 (1914).

[5] Kolloidzeitschr. **9,** 62 *et seq.* (1917).

TABLE 176

Total and Differential Heats of Swelling of Gelatine[1]

$\alpha = 87{\cdot}4$, $\beta = 0{\cdot}384$

a (amount of Water taken up per gram Dry Gelatine) in Grams.	Millimols.	Q (g. Calories) (obs.).	Q (calc.).	q.
0	0	0	0	228
0·0053	0·29	2·1	1·2	222
0·0168	0·93	5·3	3·7	209
0·0315	1·75	7·0	6·6	195
0·0406	2·25	8·9	8·3	186
0·0514	2·85	10·0	10·3	177
0·0738	4·09	13·1	14·0	160
0·1030	5·71	18·4	18·5	142
0·1070	5·94	19·1	19·0	139
0·1328	7·37	22·2	22·4	126
0·1932	10·7	30·6	29·3	101
0·2420	13·4	33·2	33·8	86

It is consistent with the view that heat of swelling is of the nature of a heat of adsorption, that the amount of heat developed is greater when we are still far removed from the maximum swelling; this appears plainly when we consider the differential coefficient of the Q, a curve, the *differential heat of swelling* q, which is likewise entered in Table 176. The differential heat of swelling is the amount of heat which is developed when a considerable amount of dry or swollen gel is allowed to take up 1 g. of liquid. The formula for q follows from equation (1), thus

$$q = \frac{a\beta}{(\beta + a)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)^2$$

The maximum value of q, which occurs when the first quantity of liquid is bound by a dry gel, may be calculated by putting $a = 0$ in equation (2), and hence

$$q_0 = \frac{\alpha}{\beta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Table 177 shows the high values obtained for q_0.

Katz arrived at very remarkable results by comparing the power of various gels to do work during swelling with the changes in their total energy. Imagine a gel swollen with water in a state 1 with the relative vapour pressure h_1 and in the state 2 with relative vapour pressure h_2. The power of doing work, that is, the difference A between the free energies (calculated on one gram) is equal to the difference in the work done in

[1] From measurements by Rosenbohm (*loc. cit.* p. 680) calculated by Katz [Kolloidchem. Beihefte **9**, 92 (1917)].

[2] According to *Katz*, instead of formulæ (1) and (2), the equations

$$Q = \frac{\varkappa a}{(\lambda + a)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1')$$

and

$$q = \frac{\varkappa(\lambda - a)}{(\lambda + a)^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2')$$

gave about as good results.

TABLE 177

Maximum Differential Heat of Swelling for various Gels

Gel.	q_0 (in gram-calories).	Observer.
Gelatine	228	Rosenbohm[1]
Agar	265	,,
Casein	265	Katz [2]
Nuclein	310	,,
Cellulose	390	,,
Inulin	420	,,
Artificial starch grains	315	Rodewald [3]
Altered wood fibre	265	Volbehr [4]

raising a piston loaded with the swelling pressure when one gram of water enters the gel in the state 1 and in the state 2; A is therefore simply equal to the difference between the swelling pressures (putting the volume of 1 gram = 1), hence according to equation (6), p. 677,

$$A = P_1 - P_2 = \frac{RT}{MV_0} \log \frac{h_2}{h_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The difference U in the total energy is equal to the difference in the heat evolution obtained when gels 1 and 2 are allowed to take up one gram of water, and is therefore equal to the difference between the differential heats of swelling

$$U = q_1 - q_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Table 178 shows that U and A are almost equal. In view of the uncertainty which is attached to the calculation of the quantities, it is not

TABLE 178

Comparison of the Differences between the Free and Total Energies during Swelling of various Gels

Gel.	a (amount of Water taken up per gram dry Gel) in Grams.	a (amount of Water taken up per gram dry Gel) in Millimols.	h.	A (in g.-cals.).	U (in g.-cals.).
Casein	0·011	0·61	0·010	25	44 (36) [5]
,,	0·029	1·61	0·022	66	64 (61)
,,	0·070	3·88	0·176		
Cellulose	0·0195	1·08	0·048	47	50 (38)
,,	0·0305	1·75	0·208	22	23 (23)
,,	0·0410	2·28	0·420		
Nuclein	0·032	1·77	0·022	66	84·5 (74)
,,	0·082	4·55	0·176	27	29 (34)
,,	0·119	6·60	0·410		

[1] *loc. cit.* p. 680.
[2] Kolloidchem. Beihefte **9**, 70 (1917).
[3] Zeitschr. f. physik. Chemie, **33**, 581 (1900).
[4] *loc. cit.* p. 680.
[5] The figures in brackets have been calculated from formula (2′), p. 681. It must be remembered that q, being a differential coefficient, cannot be determined with much accuracy, and that U is a difference of two q values.

mpossible that the agreement is in reality better. Swelling is therefore a rocess in which the change in the total energy upon taking up the liquid an be practically completely converted into mechanical work, and this takes lace by the direct instrumentality of the swelling pressure. This arises rom the fact that the power of doing work does not depend upon the kinetic nergy with which the liquid molecules strive to penetrate the gel; an smotic energy of this kind never corresponds to great thermochemical hanges. The power of doing work arises rather from the attraction of the el micellæ for the molecules of the liquid, which in view of the special tructure of gels leads directly to work being done, and upon this attraction he heat evolution naturally also depends. In spite of the similarity etween osmotic pressure and swelling pressure, there lies herein a funda- nental difference between the two. The osmotic pressure arises on account f kinetic energy, the swelling pressure as the result of potential energy.

In the equality of U and A, swelling has similarities to other processes n so-called condensed systems, that is, in systems containing no gases, but nly liquids and solids. Gels are similar in this respect to the so-called deal concentrated solutions of Nernst, for example, concentrated solutions f sulphuric acid in water. The similarity touched on above (p. 671) between gels imbibing water and the taking-up of water by sulphuric acid depends upon the very fact that in both cases it is due to the attraction of the water molecules, in the one case by the micellæ of the gel, in the other by the H_2SO_4 molecule.

Katz points out quite rightly how important this equality of U and A is for many biological phenomena. The muscles are doubtless to be regarded as machines, in which one phase of the contraction is to be regarded as a swelling process. In certain phases of muscular contraction, a very high percentage—60 per cent. and more, according to Hober [1]—of the change in total energy is converted into mechanical work; this is entirely to be expected on the grounds of the equality of U and A.

One is tempted to deduce from the equations

$$U = A$$

and

$$q_1 - q_2 = P_1 - P_2 = \frac{RT}{MV_0} \log \frac{h_2}{h_1} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

an equation

$$q_1 = P_1 = -\frac{RT}{MV_0} \log h_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This is, as Nernst [2] remarked in another connexion, not justifiable without further question. Incorporated in h_1 is the saturation pressure of the pure liquid. Therewith the validity of formula (6), in which the saturation pressure of the pure liquid cancels out, is extended up to gels at maximum swelling, and it might appear questionable whether it then still holds. Now the criticism of Nernst refers to the ideal concentrated solutions above mentioned, in the case of which, by applying formula (7), the whole range of dilute solutions is taken in. In the case of gels its application is, as Katz [3] points out, perhaps less open to objection, since with gels which swell only to a limited extent one might possibly still regard it as valid at

[1] Zeitschr. f. Elektrochemie, **19**, 738 (1913).
[2] "Lehrbuch d. physik. Chemie," 7 ed., p. 164 (cf. Tizard's English translation).
[3] Kolloidchem. Beihefte **9**, 144 (1917).

the maximum swelling. For even there—or at least close up to it—formula (2) (p. 674) holds, according to which the swelling pressure differs so entirely from the osmotic pressure in solutions in its dependence upon the concentration.

Equation (7) may therefore, following Katz, be assumed to hold. He draws from it conclusions concerning the connexion between the swelling pressure and the thermal-energetic behaviour, which was entirely confirmed. For q we have equation (2), p. 681,

$$q = \frac{\alpha\beta}{(\beta + a)^2}$$

According to (7) a similar formula should hold for P. In actual fact it is similar in nature to formula (3), p. 674, for the swelling exponent usually lies between 2 and 3. That it is not strictly equal to 2 is no contradiction, since according to equation (2′) (see note [2], p. 681) q may also be expressed by an equation in which the third power of $(\lambda + a)$ appears in the denominator. Since Q and q may be very largely represented by equations (1) and (2), employing the same exponents, it further follows therefrom that the swelling exponent k should only vary slightly from gel to gel and from liquid to liquid. This is indeed actually the case (cf. p. 674).

If the value of P from equation (6), p. 677, is substituted in (7), we get the equation

$$\frac{RT}{MV_0} \log h = -\frac{\alpha\beta}{(\beta + a)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

which represents the h, a curve (see Fig. 128). Whether a point of inflection occurs or not depends upon the ratio

$$\frac{a}{\beta} = q_0.$$

For the point of inflection

$$\frac{d^2h}{da^2} = \frac{2MV_0}{RT} q - 3 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Since q is always positive and has its maximum value in q_0, the curve with water as the liquid imbibed passes through a point of inflection if

$$q_0 > \frac{3RT}{2MV_0} = 48.$$

The larger q_0 the steeper is the rise of the h, a curve and the more pronounced is the point of inflection.

The abscissa of the point of inflection has the same value for different gels when the same liquid is imbibed; for according to (7) and (9) we have for the point of inflection

$$q = -\frac{RT}{MV_0} \log h = \frac{3RT}{2MV_0}$$

Hence for water

$$\log h = -1{\cdot}5$$

and

$$h = 0{\cdot}22.$$

The h, a curves measured by Katz actually show that the point of inflection does lie at about this vapour pressure.

Regarding some further conclusions of a similar nature, the reader is referred to the discussion of Katz.[1]

It may further be pointed out that these considerations are unquestionably valid in a wide degree also for the adsorption of gases and vapours in non-swelling gels. If they were not discussed earlier, the reason was that in their case there was no possibility of measuring the change in free energy, and hence the various consequences could not be tested.

All the thermodynamical considerations which were in part touched on earlier (p. 135) can of course be applied. The heat of swelling may be brought into relation with the temperature coefficient of the vapour pressure of the gel, just as the heat of adsorption is connected with the temperature coefficient of adsorption by equation (2), p. 135. More extended measurements on the change of the vapour pressure of swollen gels with temperature are not available. Since the heat of swelling is a positive heat change, the swelling decreases with rise of temperature. It is not easy to follow this change in swelling with rise of temperature, since peptization of the gels causes greater and greater disturbance. Hence experiments can scarcely be carried out in which the alteration in the swelling capacity, say of the maximum of swelling, with rise of temperature can be followed. Some measurements of Arisz [2] on swelling of gelatine at 10° and 20° cannot be made use of, since it is precisely in the case of gelatine that it is doubtful whether it swells to a limit or not, or whether it does not finally tend towards a sol state at every temperature.

The change in the heat of swelling itself with the temperature depends upon how greatly the specific heat of the swollen gel departs from that calculated additively from the specific heats of the dry gel and the pure liquid. In general this departure, and hence the variation of the heat of swelling with temperature, is slight.

Since the total volume becomes smaller during swelling, the latter will be favoured by rise of pressure in accordance with the principle of van 't Hoff and Le Chatelier. Naturally we are here dealing with the case in which the swollen gel is completely surrounded by walls and pressed upon by a piston impermeable to the liquid. If this is not the case, we have the quite different state of affairs which exists in the case of the swelling pressure.

The similarity between swelling pressure and osmotic pressure also appears in the fact that a liquid contained in a gel has a lower freezing-point than the pure liquid in consequence of the swelling pressure. According to Polanyi [3] we have for the depression Δ of the freezing-point

$$\Delta = \frac{PV_0T_0}{Q' + S} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Here V_0, T_0 and S are specific volume, melting-point, and latent heat of fusion (referred to 1 gram) of the pure liquid ; Q' is the total heat of swelling referred to 1 gram of liquid. The equation holds in this form only for small swelling pressures and depressions of the freezing-point in the immediate neighbourhood of the maximum swelling. If we wished also to apply it at larger pressures, it would be necessary to take into account the depend-

[1] Kolloidchem. Beihefte **9**, 111 *et seq.* (1917).
[2] *loc. cit.* p. 655.
[3] Zeitschr. f. physik. Chemie, **88**, 627 (1914).

ence of the heats of swelling and of fusion on temperature and to integrate. The depression of the freezing-point thus produced may be considerable. An approximate calculation may be carried out from Katz's data. For casein he determined both the vapour-pressure isothermal and the heat of swelling. For $a = 0{\cdot}011$ g., the relative vapour pressure is 0·01, the swelling pressure according to formula (6), p. 677, about 6,070 atmospheres. Since the heat of swelling for the value $a = 0{\cdot}011$ was not measured, it must be calculated from formula (1), p. 680; for casein $\alpha = 3{\cdot}83$ and $\beta = 0{\cdot}145$, hence $Q = 2{\cdot}701$ cal, $Q' = 245{\cdot}5$ cal. If the fact is neglected that these measurements were carried out at room temperature, and not at 0°, we obtain a depression of the freezing-point of 120°.

We may consider this circumstance to be in part responsible for the fact that organized structures containing little water, such as seeds, bacteria, and the like, are able to support very low temperatures, such as that of liquid air, without their vitality being injured.[1] A kinetic influence is probably more important than this static one; the water molecules are so bound, and deposited in amicronic capillaries, that the molecular arrangement necessary to the formation of the smallest ice crystal occurs far less frequently than in the free liquid. The supercooling is much greater.

In the foregoing considerations matters were simplified by the tacit assumption that gels are composed of micellæ of one kind only; that they are monodisperse. In reality everything is much more complicated, at least with many gels, particularly the gelatine gels most investigated. These are without doubt polydisperse, which fact sensibly influences both swelling equilibrium and swelling velocity. This point can only be dealt with when the polydisperse behaviour in the transformation of gelatine sols into gels has been considered more closely (cf. p. 708).

Adsorption by Gels

Swelling of gels in pure liquids is comparatively well understood, thanks particularly to the investigations of Katz. Our knowledge becomes very uncertain, however, when we come to swelling in solutions. The causes of this fact are manifold. One is unmistakable, namely, that the binding to the micellæ will depend greatly upon the competition between the molecules of the solvent and of the solute. The adsorption of the solvent takes effect on a scale quite different from that in the case of adsorption by non-swelling adsorbents. Hence before we turn to swelling in solution, we must first consider in a few respects adsorption by gels.

As regards adsorption by non-elastic gels there is little new material to be added, for the adsorbents most particularly discussed, such as charcoal, kaolin, and many others, are none other than the non-elastic xerogels. It will be remembered that according to Patrick's[2] experiments, adsorption of carbon dioxide and sulphur dioxide by dry SiO_2 gels entirely obeys the laws of adsorption. Here also at higher pressures below the critical temperature the condensation of the gas to liquid in the capillaries is observed. The conclusion as to the diameter of the capillaries is apparently not so definite in the case of SO_2 as with the liquids used by J. S. Anderson (see p. 666), perhaps because the thickness of the adsorption layer in the neighbourhood of the critical temperature is larger and more variable than at a

[1] See on this point e.g. *Pfeffer*, "Pflanzenphysiologie," 2nd Ed., p. 297 *et seq.* (1904).
[2] *loc. cit.* p. 127.

greater distance therefrom as in the case of the liquids. According to formula (1), p. 664, indeed, we do not calculate directly the radius of the capillaries, but the radius of curvature of the meniscus. The two magnitudes only coincide when the thickness of the adsorption layer only constitutes a small and negligible fraction of the diameter of the capillaries. The taking-up of ammonia by silicic acid gels (Patrick, *loc. cit.*) does not fully correspond to an adsorption; the slowness of the attainment of equilibrium points to a sorption, doubtless to a chemical interaction.

Similar facts are true for adsorption in solutions. Qualitative experiments by Zsigmondy [1] show that SiO_2 gels unmistakeably adsorb dyes, and further, that acid dyes appear to be taken up weakly and reversibly, in accordance with the negative charge of the SiO_2, and basic dyes strongly and doubtless with exchange adsorption.

In adsorption by these gels the fine capillary structure shows itself. It is indeed the reason why such gels may be used as ultra-filters (cf. p. 379), and this ultra-filter action is also of significance for adsorption; for only those dissolved substances which have molecules sufficiently small to penetrate without hindrance into all capillaries will permeate the gel uniformly and be adsorbed according to the total surface, inner and external. The large molecules of substances of high-molecular weight and the micellæ of colloidal solutions will not be able to do this; they are held back at the surface of the gel, while the water alone passes into its interior. This was clearly observed by Zsigmondy [2] on silicic acid gels. The particles of a silver sol coated only the surface of a gel with a mirror. Ferric hydroxide, benzopurpurin, and casein likewise only collected at the surface. These experiments again illuminate clearly the fact already mentioned (p. 171), that the adsorption of substances of high-molecular weight by adsorbents such as cocoanut charcoal depends upon the pores being large enough for the inner surface to be reached by the dissolved molecules (cf. also p. 217).

A very different state of affairs may occur with the swelling gels. Not in the case of gas adsorption—this obeys, as far as experience goes, the usual laws [3]—but with adsorption in solution. Swelling gels are adsorbents in which negative adsorption has been observed with unusual frequency. The old experiment of Ludwig [4] so often cited, that pigs'-bladder in a cold saturated solution of common salt may raise the concentration to such an extent that the salt crystallizes out, is an example of such adsorption. The same observation is described by Dumanski [5] with gelatine in a K_2SO_4 solution. R. O. Herzog [6] has further remarked that in the adsorption of dextrose by weakly chromated hide powder the rotation increases sensibly; likewise in adsorption by the same adsorbent the concentration of a neutral ovalbumin solution increases by about 7 per cent.: in adsorption of a dextrose solution by tanned gelatine an increase in concentration from 27·8

[1] "Kolloidchemie," 3rd Ed., p. 235. Further also *Tschermak*, Zeitschr. f. physik. Chemie, **53**, 349 (1905). *Herm. Ambronn*, comm. by *E. Küster*, Ber. d. deutsch. botan. Ges. **15**, 136 (1917).

[2] "Kolloidchemie," 3rd Ed., p. 236.

[3] See, e.g., concerning adsorption of various gases by caoutchouc, *Reychler* [Journ. Chim. Phys. **8**, 3, 627 (1910)]; *Austerweil* [Compt. rend. **154**, 196 (1912)], and others.

[4] Pogg. Ann. **78**, 320 (1849); Zeitschr. f. rationelle Medizin von *Henle* and *Pfeufer*, **8**, 19 (1849).

[5] Zeitschr. f. physik. Chemie, **60**, 559 (1907).

[6] Zeitschr. f. physiol. Chemie, **57**, 315 (1908); *R. O. Herzog* and *Adler*, Kolloidzeitschr. **2**, II Suppl. p. III (1908); see also *Berczeller*, Biochem. Zeitschr. **90**, 290 (1918) (Negative adsorption of sugar by starch and serum albumin).

to 30·7 per cent. was observed. According to McBain [1] we must likewise regard the increase in alkali concentration which occurs upon the salting-out of a soap solution with alkali as a negative adsorption, since the soap (or acid soap) jelly separating out removes so much water from the solution.

Herzog leans towards the view that it is essential to the appearance of negative adsorption that the gel should be to a large extent semi-permeable, and allow the molecules of water to pass through, but not the molecules of solute, and regards as a confirmation of this view the fact that in the experiments above mentioned only gelatine tanned by formaldehyde and hence less permeable showed negative adsorption, and not untanned. But according to Stiasny [2] this is not generally correct; negative adsorption in a solution of egg albumin by non-chromated hide powder is stronger than by chromated. It is now highly probable that with these gels negative adsorption also occurs even when the solute can reach the inner surface unhindered. The adsorption of water by these hydrophilic gels is very strong, and hence it is possible that we may enter the range of concentration in which water molecules are taken up in preference to solution molecules (see Fig. 35, p. 181).

Naturally, normal positive adsorption is met with in the case of many substances and with small concentrations; it very largely obeys the adsorption laws according to the experiments of Herzog and his co-workers,[3] which were carried out with hide powder in particular. In other cases, for instance in the taking-up of hydrochloric acid by hide powder, pure chemical processes appear to preponderate.[4]

A consideration of dyeing, tanning, and allied phenomena, in which adsorption by swelling gels plays an important part, should now follow. But since in this connexion the question of the arrangement and state of aggregation of the micellæ is not without significance, these phenomena will be dealt with later (p. 753).

Swelling in Solutions

Our comparatively scanty knowledge of the adsorption of the molecules of solvents and solutes by swelling gels is not the only difficulty which prevents our understanding of swelling in solutions. The purely experimental difficulties are likewise great. Thus E. Posnjak [5] could not succeed in measuring the swelling pressure of gelatine in aqueous salt solutions with the meter above described (p. 673). The peptizability of the gelatine, already sensible in aqueous solutions, becomes so strong, even in a solution of Na_2SO_4, that the observed change in volume does not allow the amount of water taken up to be deduced. With a salt such as KCNS the peptization was such that in a 2N solution the disc of gelatine was completely dissolved colloidally out of the porous cell in a few hours.[6] The measurements, upon which it was earlier supposed that reliance could be placed, were carried

[1] *McBain* and Miss *Taylor*, Journ. Chem. Soc. **115,** 1300 (1919).

[2] From "Der Gerber," 1909; cited from Kolloidzeitschr. **6,** 57 (1910).

[3] *loc. cit.* p. 687; further *R. O. Herzog* and *Rosenberg*, Kolloidzeitschr. **7,** 222 (1911).

[4] See e.g. *Kubelka*, Kolloidzeitschr. **19,** 172 (1916); **23,** 57 (1918).

[5] Kolloidchem. Beihefte **3,** 440 *et seq.* (1912).

[6] Also *M. H. Fischer* [Kolloidzeitschr. **17,** 1 (1916)] and further *M. H. Fischer* and *Coffman* [Journ. Amer. Chem. Soc. **40,** 303 (1918)] point out that swelling and peptization are independent of one another.

out by measuring the maximum swelling in salt solutions.[1] The weighed gelatine plate was dipped into the solution and the increase in weight determined from time to time with suitable precautions, and extrapolated to the final equilibrium. I cannot but suppose that here too loss in weight by peptization of the gel renders these measurements erroneous.[2] They will therefore only be discussed here with great reservation. Scarcely any investigation would so materially add to our knowledge of biological processes, as reliable measurements on the influence of dissolved foreign substances, especially electrolytes upon swelling in water; measurements of the swelling pressure would be more trustworthy than those of the maximum swelling alone. The distribution of the solute between gel and external liquid would of course have always to be determined at the same time. And very particular attention would have to be paid to the H· ion concentration, since its influence is often decisive.

A further method, that gives qualitatively or semi-quantitatively a satisfactory picture of swelling in solutions, is frequently applied by M. H. Fischer.[3] The powdered gel is placed in a graduated test-tube, and covered with the liquid to be imbibed. It swells to a jelly-like mass, and the height to which it rises is a measure of the amount of liquid taken up. Lüers and M. Schneider [4] show that this method largely agrees with that of Hofmeister. In agreement with both stands a third method used by Wo. Ostwald.[5] By this he measures with a viscosimeter the change in velocity of flow of a liquid when suspended particles swell in it.

The swelling of gelatine depends in the highest degree upon the H·-ion concentration.[6] According to Chiari [7] it has a minimum at the isoelectric point of the gelatine, therefore at a p_H [8] of 4·7, and increases at first strongly with increase both of H· and of OH′-ion concentration. It thus comes about that a gel moistened with alkali or acid and already somewhat swollen, when brought into pure water swells much more strongly than one not so treated. From the older experiments it would appear that with different acids the lyotropic series makes itself felt. According

[1] *Hofmeister*, Arch. f. exp. Pathol. u. Pharmakol. **28**, 210 (1891); further **27**, 395 (1890); *Pauli*, Pflüg. Archiv, **67**, 219 (1897); **71**, 1 (1898); *Spiro*, Beitr. z. chem. Physiol. u. Pathol. **5**, 276 (1904); *Wo. Ostwald*, Pflüg. Archiv, **108**, 563 (1905); **111**, 581 (1906); *R. Ehrenberg*, Biochem. Zeitschr. **53**, 356 (1913); *M. H. Fischer* and Miss *Sykes*, Kolloidzeitschr. **14**, 215 (1914); **16**, 129 (1915); Miss *Hooker* and *M. H. Fischer*, *ibid.* **26**, 49 (1920); *M. H. Fischer* and Miss *Hooker*, Journ. Amer. Chem. Soc. **40**, 272 (1918); *M. H. Fischer* and *Benzinger*, *ibid.* **40**, 292 (1918); *Lenk*, Biochem. Zeitschr. **73**, 15, 58 (1916); *Tolman* and *Stearne*, Journ. Amer. Chem. Soc. **40**, 264 (1918); *Tolman* and *Bramwell*, *ibid.* **41**, 1503 (1919).

[2] *Wo. Ostwald* (*loc. cit.*, foregoing note) discusses this source of error several times. He does not seem to have tested, however, how large the quantity peptized actually is, and whether it does not suffice to affect the accuracy of the results very adversely.

[3] *M. H. Fischer* and Miss *Moore*, Amer. Journ. of Physiol. **20**, 230 (1907); Kolloidzeitschr. **5**, 197 (1909); *M. H. Fischer*, Pflüg. Archiv, **125**, 99 (1908); further *M. H. Fischer*, "Das Ödem," Dresden, 1910, p. 22 *et seq.*

[4] Kolloidzeitschr, **28**, 1 (1921).

[5] Pflüg. Archiv, **108**, 586 (1905); Kolloidzeitschr. **12**, 213 (1913).

[6] Proved for gelatine by *Spiro* [Beitr. z. chem. Physiol. u. Path. **5**, 276 (1904)] and *Wo. Ostwald*, *loc. cit.* under [1]; and for gelatine and fibrin by *M. H. Fischer* (*loc. cit.* under [1]).

[7] Biochem. Zeitschr. **33**, 167 (1911).

[8] These values are, as well known [see *Sörensen*, Biochem. Zeitschr. **21**, 134 (1904)], the exponents with sign reversed, to which the base 10 must be raised, in order to obtain the H·-ion concentration existing in the solution in question.

to later investigations of J. Loeb [1] this is not, or only very conditionally, the case; and the variation in this sense disappears completely when the dependence upon the H·-ion concentration existing in the gel itself is taken into account. He followed the swelling of gelatine in various acids according to a method similar to that of M. H. Fisher, but took particular account, as we have said, of the H·-ion concentration in the gel itself. This was measured by washing the gel, which was in equilibrium with the acid, carefully upon a filter, then dissolving it in excess of water by warming, and measuring the H·-ion concentration of this sol. It was found that the swelling increased from its minimum at the isoelectric point as the H·-ion concentration increased to a maximum at $p_H = 3{\cdot}2$, and then decreased again. The curves for nitric, trichloracetic, hydrochloric, phosphoric, and oxalic acids practically coincided; that for sulphuric acid lay somewhat lower, but the maximum appeared at the same H·-ion concentration as in the other cases. Acetic acid gave a curve which differed somewhat; the swelling increased more rapidly, and apparently also to beyond the usual maximum.

One might think that the salt-like compound of gelatine with H_2SO_4 is less dissociated than the compounds of gelatine with the other acids, and that the swelling in H_2SO_4 is then less, since the power of taking up water is of course connected with the number of ions present. But an investigation of the conductivity showed that the difference in the conductivity—in its dependence upon the H·-ion concentration—with gelatine-sulphuric, gelatine-oxalic, and gelatine-hydrochloric acid solutions is very slight, and that it does not therefore explain the greatly different behaviour of sulphuric acid during swelling. Nor is it any more possible to interpret the decrease in swelling below $p_H = 3{\cdot}2$ by the dissociation of the compound gelatine-acid being depressed at higher acid concentrations; the conductivity shows nothing of the kind.[2]

But a parallelism certainly exists between the dependence of the swelling on the H·-ion concentration and that of the *osmotic pressure* of gelatine sols containing acid on the same quantity.[3] This connexion cannot yet be satisfactorily explained. J. Loeb supposes that the decrease of the osmotic pressure at high H·-ion concentrations, and also that caused by neutral salts, are connected with electrosmotic processes, which appear in quite a similar manner when, instead of a gelatine solution, the acid or salt solution fills the interior of the collodion bag.

The behaviour of gelatine as regards swelling in alkaline solution was similar; then also there was a sensible difference between alkalis with univalent kations and those with bivalent.

As regards swelling in salt solutions, there are as yet no measurements available in which swelling was compared at constant H·-ion concentration. The following data can therefore only be made use of with caution. The lyotropic series of the ions becomes evident. This is seen in the first place with the anions: in thiocyanate [4] and iodide solutions. Many gels swell more strongly than in chloride solutions, and in these again more strongly than in sulphates. The direction in which swelling in salt solutions differs from that in pure water cannot be stated so definitely. From Hofmeister's

[1] Journ. of General Physiol. **3**, 247 (1920).
[2] *J. Loeb, loc. cit.* under [1].
[3] *J. Loeb, ibid.* **1**, 559 (1918–19); **2**, 273 (1920); **3**, 85 (1920).
[4] See *Meusel*, "Ueber die Quellkraft der Rhodanate und die Quellung als Ursache fermentartiger Reaktionen." Gera, 1886.

experiments, particularly those on pig's-bladder, and Wo. Ostwald's on gelatine, it would appear to follow that, compared with pure water, sulphates hinder swelling, chlorides, nitrates, and bromides assist it. Here, it is true, the source of error already mentioned, peptization, might have a disturbing effect. Should the swelling produced by sulphate solutions be but little greater than that produced by pure water, while on the other hand they peptize more strongly, the observed swelling effect might very well be apparently depressed below that of pure water. But perhaps experiments by Dumanski [1] on the electrical conductivity of salt solutions in gelatine gels (which experiments, it is true, greatly need extension) tell in favour of a contrast between chlorides and sulphates, or more correctly, between KCl and K_2SO_4. For he found a distinct negative adsorption with K_2SO_4, which in any case only slightly assists swelling, and in a certain fashion hinders it ; while KCl, which favours swelling, did not show any such negative adsorption.

Wo. Ostwald describes a very complicated dependence of the maximum swelling upon the electrolyte concentration, for example, with a maximum in the case of $NaNO_3$ and NH_4NO_3, and a maximum and subsequent minimum (as the concentration increases) with KCl. One would prefer to regard these results also as valid only when we know that they are not caused by the superposition of the effects of swelling on those of peptization. Lenk [2] did not observe such a complicated connexion between swelling and electrolyte concentration. Perhaps the heavier gelatine plates which he used diminish the source of error due to peptization. It is true that his results cannot be compared directly with those of Wo. Ostwald, as the latter rightly points out,[3] since he did not work with dry, but with water-swollen plates, and generally did not wait for the maximum swelling.

The lyotropic series of kations appears to be less pronounced.

Particularly important is the question of swelling in *mixtures of electrolytes*, since it is not impossible that the peculiarities in the biological action of salts, as considered on p. 648, frequently also depend upon antagonistic ionic effects appearing in the displacement of swelling equilibria.

Effects of this kind are actually observed in the swelling in mixtures of electrolytes. Thus, as M. H. Fischer [4] and Pauli and Handovsky [5] have shown, the strong swelling of fibrin and gelatine in acids is depressed by addition of salts, obviously because competition for the water takes place between ions and swelling substance. Corresponding to this we have the widely extended lyotropy of this influence ; additive action of the ions, prominence and distinct lyotropic order of the anions. That the lyotropic order of kations and anions often appears displaced is not surprising, since the measurements were frequently not strictly comparable. HCl, for instance, was taken as acid imbibed ; the addition of a salt with another anion produces by double decomposition a second acid, which does not have such a strong swelling action as HCl. In order to compare the kations, the salt must be used in conjunction with the acid having the same anion. In order to compare the anions, mixtures of acid should be used. Experiments by Lenk on electrolyte mixtures do not appear to me, for the reasons given above, to be free from objection.

[1] Zeitschr. f. physik. Chemie, **60,** 553 (1907). [2] *loc. cit.* p. 689.
[3] Biochem. Zeitschr. **77,** 329 (1916).
[4] *loc. cit.* p. 688 ; further *Upson* and *Calvin,* Journ. Amer. Chem. Soc. **37,** 1295 (1915).
[5] Biochem. Zeitschr. **18,** 340 (1909) ; **24,** 239 (1910).

The influence of electrolytes upon swelling in acids is so considerable that a gelatine carefully purified from electrolytes is far more sensitive towards a slight rise in the $H^{\cdot}$-ion concentration of the water, than ordinary commercial gelatine. With the purified gelatine, the CO_2 content of distilled water produces sensibly greater swelling than that in conductivity water (Chiari [1]).

An ionic antagonism connected with hydration has already been described in the case of the coagulation of sols, such as Odén's sulphur sols or lecithin sols (p. 647). That here observed in the case of swelling should depend upon similar causes.

M. H. Fischer [2] inclines to the view that the absorption of water by the protoplasm of cells is frequently, if not predominantly, to be ascribed to the swelling of proteins, and less to an osmotic effect of semi-permeable membranes. The similarity in the absorption of water by frog muscles and the eyes of animals from solutions of various acids is in fact so great that in these cases one can hardly doubt that it is due to swelling. This naturally does not exclude its being a matter of more or less pure osmotic effects in other cases. On the ground of the strong swelling of proteins in acids M. H. Fischer attempts to explain a series of pathological phenomena, for example, the œdema in cases of heart- and kidney-disease. He assumes the formation of an unusual amount of acid in the tissues in question, resulting in very strong swelling. It is however questionable whether this explanation is true in its general form ; in the first place formation of acid is not observed in the diseases in question, and in the second, the changes which the organs in question experience in the case of œdema are different in kind from the case of swelling in acid.[3]

The influence of non-electrolytes upon swelling must also be taken into account. Substances containing many hydroxyl groups, such as sugar, in the case of which a decided attraction for water has to be reckoned with, again appear to adversely affect swelling. Experiments in this direction were originated by Hofmeister. The swelling of fibrin in acid, according to M. H. Fischer,[4] is not influenced by substances such as glycerine, urea, dextrose, and sucrose, while the swelling of gelatine in hydrochloric acid is distinctly favoured by urea.[5]

Colloidal solutions are in general without sensible influence upon swelling. This is true, according to Spiro,[6] for gelatine in As_2S_3 and other sols. Commercial Fe_2O_3 sols appreciably favour swelling, but only by their $FeCl_3$ content ; the HCl formed by hydrolysis exerts an acid effect. The carefully dialysed sol does not favour swelling.

In the case of swelling in solutions we also have to take into account a series of thermodynamic consequences, by which in particular the adsorption of solvent and solute is connected with the swelling pressure. Only an argument due to Polanyi,[7] which is nothing more than the application to the case of an imbibing gel of the consideration holding for the deduction

[1] *loc. cit.* p. 689.

[2] Particularly " Das Ödem," Dresden, 1910 ; see also Science, **48,** 143 (1918).

[3] See *Schade,* " Die physikalische Chemie in der inneren Medizin," Dresden and Leipzig, 1920, p. 381 *et seq.*

[4] " Das Ödem," p. 29 ; *loc. cit.* under [2].

[5] " Das Ödem," p. 47 *et seq.*

[6] *loc. cit.* p. 689.

[7] Biochem. Zeitschr. **66,** 258 (1914) ; Zeitschr. f. physik. Chemie, **88,** 622 (1914).

of the Gibbs adsorption formula (cf. p. 46), will be discussed at length. Let a gel of swelling pressure P and volume V be in equilibrium with a solution of concentration c, osmotic pressure P and volume V. Let gel and solution above it be between two pistons. Let the lower piston II be impermeable to the gel only, but permeable to solvent and solute ; with the aid of it, therefore, work may be done against the swelling pressure. An upper piston I is only permeable to the solvent ; by its aid work may be done against the osmotic pressure. If by means of the upper piston I solvent to the amount dV is pressed out, the work $-PdV$ is done against the osmotic pressure. The swelling pressure is thereby changed to

$$P + \left(\frac{\delta P}{\delta V}\right)_V dV$$

If now the lower piston II is forced down by dV, the work

$$-\left[P + \left(\frac{\delta P}{\delta V}\right)_V dV\right]dV$$

is done. The osmotic pressure thereby changes to

$$P + \left(\frac{\delta P}{\delta V}\right)_V dV.$$

For the liquid pressed out has a different concentration from that originally present between the two pistons. Piston I is brought back to its original position with gain of the work

$$+\left[P + \left(\frac{\delta P}{\delta V}\right)_V dV\right]dV$$

and likewise piston II with gain of the work $+ PdV$. Since the cycle is isothermal we have

$$-PdV - \left\{P + \left(\frac{\delta P}{\delta V}\right)_V dV\right\}dV + \left\{P + \left(\frac{\delta P}{\delta V}\right)_V \delta V\right\}dV + PdV = 0,$$

hence

$$\left(\frac{\delta P}{\delta V}\right)_V = \left(\frac{\delta P}{\delta V}\right)_V \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Since we wish to know the dependence of P upon the concentration c, we write

$$\frac{\delta P}{\delta c}\,\frac{\delta c}{\delta V} = \frac{\delta P}{\delta c}\,\frac{\delta c}{\delta V} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and discuss the single differentials,

$$\frac{\delta P}{\delta c} = RT.$$

For c we again put (cf. p. 47)

$$c = \frac{n - aV}{V}$$

by putting the adsorbent surface of the gel proportional to the volume V. Then

$$\frac{\delta c}{\delta V} = \frac{n - aV}{V^2}$$

and

$$\frac{\delta c}{\delta V} = -\frac{a}{V}$$

From (2) it follows that

$$a = \frac{c}{RT}\,\frac{\delta P}{\delta c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

That is to say, if a is positive, if the solute is positively adsorbed (more strongly than the molecules of the solvent), then $\frac{\delta P}{\delta c}$ is positive; the swelling pressure increases with the concentration of the solute, the positively adsorbed substance favours swelling; while, conversely, a negatively adsorbed substance hinders it. One may hope to find this rule confirmed when swelling in solution leads to definite equilibria not disturbed by the peptization of the gel. Dumanski's experiments mentioned above (p. 691) may perhaps already be interpreted in this sense.

The Velocity with which Liquid is taken up in Gel Structures. The Swelling Velocity

The rate at which liquid is taken up by non-swelling or only slightly swelling gels will first be considered. The majority of such experiments relate to the rate of rise of liquids in strips of filter paper, as is repeatedly observed in Goppelsröder's capillary analysis (cf. p. 214). If we are sufficiently removed from the final state of equilibrium, the height h reached by the liquid in the time t may be to a great extent expressed by an equation

$$h^a = kt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which the exponent a is not far removed from 2.

Bell and Cameron[1] were the first to point out that the velocity with which a liquid rises in a gel skeleton is governed by the same laws as hold for the motion in a capillary according to Poiseuille. In view of the fineness of the capillaries in the gel structure and the resulting height of capillary rise we can assume that we are, as in the case of equation (2), p. 84, so far removed from equilibrium that the driving force may be regarded as constant. The length of the thread of liquid is here equal to the height h of the liquid in the gel at the time t. Hence we have

$$\frac{dh}{dt} = kh$$

and

$$h^2 = kt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

an equation which agrees with formula (1) since a usually only differs but little from 2.

The investigators named confirmed the formula first for the rise of liquid in filter paper and for cylinders filled with particles of soil. Wo. Ostwald[2] then calculated Goppelsröder's measurements on the basis of this formula.

Table 179 gives an example of the validity of formula (1).

The velocity with which liquid is taken up by swelling gels, the swelling velocity (abbreviated S.V.), has usually been measured in a different manner. Data applicable to its calculation are necessarily obtained in measuring the maximum swelling, since in doing so the increase in weight of the gel has to be determined from time to time. In measurements of the swelling pressure by E. Posnjak's method (p. 673) various readings and hence various amounts of imbibed liquid are also found from time to time before the state of equilibrium is reached; but since in the apparatus in question the liquid

[1] *loc. cit.* p. 84.

[2] Kolloidzeitschr. **2**, Suppl. II, p. XX (1908); further *Lucas, ibid.* **23**, 15 (1918).

TABLE 179

Rate of Rise of Water in Filter Paper

$k = 966{\cdot}1$; $a = 3{\cdot}448$

t (in minutes).	h (obs.).	h (calc.).
30	19·8	19·7
60	24·1	24·1
240	36·4	36·1
300	38·6	38·4
360	40·5	40·5
420	41·7	42·5
480	43·6	44·0

also has to pass through the walls of the porous cell before it reaches the gel, these measurements do not allow the actual swelling velocity to be measured. This objection applies less to the experiments of Reinke,[1] which were carried out with the œdometer, since the holes through which the liquid penetrates are considerably wider.

We are therefore in possession of fairly comprehensive data concerning the swelling velocity. The observations already made, casually as it were, by Hofmeister,[2] Reinke,[3] and others may be utilized in this direction. Then Flusin [4] measured swelling velocities exclusively, not on aqueous gels, but on caoutchouc in organic liquids. The time-course is frequently simpler than might at first be expected with such a complicated phenomenon. As Pascheles [5] first showed from Hofmeister's measurements on glue and agar jellies, the ordinary equation for a unimolecular reaction holds widely:

$$\frac{da}{dt} = k(a_\infty - a)$$

Integrated,

$$k = \frac{1}{t} \log \frac{a_\infty}{a_\infty - a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In these equations a is the amount of liquid taken up at time t, a_∞ that at maximum swelling.

In Table 180 experiments by Reinke on a Laminaria leaf only 0·1 mm. thick have been calculated according to formula (3).

Hence also for the swelling velocity we have the regularity, so frequent in velocity processes, that the process goes on the faster, the further we are removed from equilibrium.

This regularity probably only holds provided that the imbibing layer is thin enough. Only then will the gel swell practically as a whole, and be as a whole at a definite distance from equilibrium at any moment. When, on the other hand, thick layers of gel swell, the external layers are heavily swollen, the internal ones only slightly altered. This takes effect, for example, in the change of the refractive index from outside inwards, which may also be tested on swelling glue-jellies, and further in the change of form which

[1] *loc. cit.* p. 673.
[2] Arch. f. exper. Pathol. u. Pharmakol. **27**, 395 (1890).
[3] *loc. cit.* p. 673.
[4] Ann. d. chim. et d. phys. (8), **13**, 480 (1908).
[5] Pflüg. Archiv, **67**, 219 (1897).

TABLE 180

Swelling Velocity of a Laminaria Leaf in Water

Room temperature

t (in minutes).	a (in per cent. by Volume of the dry Material)	k.
1	40	0·108
3	96	0·094
5	143	0·091
7	183	0·090
9	216	0·089
11	246	0·090
13	270	0·090
15	294	0·093
18	326	0·099
20	345	0·106
22	360	0·114
24	372	0·121
∞	392	—

thicker layers of gel experience during swelling [1]; the large surfaces of rectangular gelatine blocks are at first deformed so as to be concave towards the outside, and the block only reassumes its original form with plane surfaces when swelling is uniform throughout the mass. A simple course according to formula (1) is then not to be expected. Perhaps the fact that in Flusin's [2] experiments the formula does not hold depends upon his use of thicker plates of caoutchouc (over 1 mm.).[3]

His measurements of the S.V. of caoutchouc in various organic liquids show that S.V. and swelling equilibrium (hence maximum swelling) are independent of one another. Unfortunately Flusin did not always extend his experiments to the point of definite arrival at maximum swelling. But the state of swelling which he reached in 24 hours was, as we can see from the course of the curves, not too far removed from the maximum. If we compare the amount of liquid taken up after 1 minute with that taken up after 24 hours, as has been done in Table 181, we see how, for instance, caoutchouc swells in chloroform only slightly less strongly than in carbon disulphide, while the S.V. in chloroform is far less than in carbon disulphide; in the same way it swells about twice as strongly in benzene as in ethyl ether, while the S.V. in the two liquids is about equal.

The S.V. increases with temperature, but usually not greatly. According to F. Kirchhof [4] the S.V. of vulcanized caoutchouc in benzene increases 1·09 times between 40° and 50°. Here also a contrast exists between S.V.

[1] *Arisz, loc. cit.* p. 655.

[2] *loc. cit.* p. 669.

[3] The departure is in the sense that equation (1) might hold. It would be worth testing whether this might not be true under certain circumstances also for swelling gels. Thus *Brailsford Robertson* [Journ. Phys. Chem. **14**, 377 (1910)] believes that the velocity of dissolution of casein in alkalis may be referred to a swelling velocity as the slowest process concerned. For the amount x dissolved in time t the equation $k = \frac{x^a}{t}$ holds; the velocity increases with the superficial area of the casein and only slightly with temperature rise.

[4] Kolloidchem. Beihefte **6**, 1 (1914).

TABLE 181

Maximum Swelling and Swelling Velocity for Vulcanized Caoutchouc in various Liquids

t = 16°

Liquid.	Amount of Liquid taken up in 1 minute (millimol per gram Caoutchouc).	Amount of Liquid taken up in 24 hours (millimol per gram Caoutchouc).
Carbon disulphide . . .	10·8	135
Chloroform	4·1	121
Toluene	2·3	69·9
Benzene	1·9	66·4
Ethyl ether	1·8	33·3
Xylene	1·25	52·0
Chlorbenzene	0·67	43·3
Nitrobenzene	0·19	13·1

and swelling equilibrium, since the latter is but little displaced by temperature, and in the opposite sense.

The connexion between S.V. and osmosis discovered by Flusin (*loc. cit.*) is noteworthy. The latter was measured by the following arrangement. The membrane M of the gel in question is stretched vertically between two vessels A and B, which fit well together ; in order that it may not become curved (which can cause very serious disturbances) it was held between two stiff sieves of platinum or nickel. A and B end in horizontal capillary tubes provided with graduations. By observing the motions of the liquid in these capillaries the quantity passing through the membrane in a given time can be determined.

The connexion between the S.V. and the velocity of osmotic permeation of the membrane (abbreviated O.V.) is particularly clearly seen in the experiments carried out with a caoutchouc membrane. In these the vessel A was filled with liquid, e.g. ethyl alcohol, causing only slight swelling, the other with a liquid, such as chloroform or benzene, causing strong swelling. Liquid then passed from B to A, and the amount passing over in a given time (O.V.) was very nearly proportional to the amount of liquid which the membrane would have taken up in the same time upon swelling in the active liquid in question (cf. Table 182). The values of O.V. are all recalculated for a time of one hour and a membrane surface of 100 sq. cm.

If the weakly acting liquid in A is replaced by another with an equally weak action, the quantity of liquid passing over into the latter in a certain time remains proportional to the S.V.

This behaviour is entirely intelligible. The more rapidly the membrane swells, the more liquid can pass from one side of the membrane to the other.

When two different but less active liquids were used with the caoutchouc membrane, the rule held generally that the liquid imbibed more rapidly by the membrane passed over preferentially to that which the membrane imbibed less rapidly.

In full agreement with this was the behaviour of purely hydrophilic membranes, such as pig's-bladder, when one side was in contact with water,

TABLE 182

Comparison of Swelling Velocity and Rate of Osmosis with a Membrane of Vulcanized Caoutchouc

$t = 16°$

Liquid.	S.V. millimol Liquid taken up by 1 gram Caoutchouc in 1 min.	O.V. (millimol).	$\frac{O.V.}{S.V.}$
Carbon disulphide	10·8	277	25·5
Chloroform	4·1	156	38
Toluene	2·3	61	27
Benzene	1·9	55	28·5
Ethyl ether	1·8	63	35
Xylene	1·25	35	28
Chlorbenzene	0·67	11	17
Nitrobenzene	0·19	2·4	12·5

and the other with an aqueous solution. In the majority of cases normal positive osmosis is observed, that is to say, the water passes through the membrane into the solution. In this case Flusin also always found that the water is to be regarded as the more active liquid; the membrane swelled more rapidly in pure water than in the solution. He did not content himself with the fact that the fresh membranes swelled more rapidly in pure water, but again tested their S.V. in pure water after they had swollen in the solution, and the dissolved substance had then been carefully washed out. When again brought into pure water, the membranes frequently swelled more rapidly than they did the first time.

Now solutions exist in which a decided *negative osmosis* takes place. The solution passes over into the pure water. Flusin observed it with dilute solutions of acetic acid and tartaric acid and thus confirmed the older experiments of Dutrochet [1] and Th. Graham,[2] who had also found negative osmosis when using pig's-bladder membranes and dilute acids; further also with solutions such as $FeCl_3$ and $AuCl_3$, which split off acid hydrolytically. The dependence of this negative osmosis upon the acid concentration, found by Flusin, is remarkable. With increase in concentration it reaches a maximum, then decreases, and with large concentrations we have the normal positive osmosis. Flusin was able to explain this peculiar behaviour in so far as he showed that the S.V. runs parallel with the osmosis; as opposed to other electrolyte solutions, the pig's-bladder swells more rapidly in dilute acid than in pure water, even when after swelling in the acid the latter is washed out and the membrane again placed in pure water. The dilute solution of acid is thus the more active liquid, and in complete agreement with the rule stated above the liquid passes by osmosis from the active liquid, the acid solution, to the less active, pure water. In concentrated acid solution the pig's-bladder swells more slowly than in pure water.

This behaviour is illustrated numerically in Table 183. In it we have, besides the concentration c of the tartaric acid, the change of volume of the solution V_b—recalculated for one hour's duration of osmosis and a membrane surface of 100 sq. cm. It is positive when the volume of the

[1] *loc. cit.* p. 268. [2] *loc. cit.* p. 268.

olution increases, when therefore with positive osmosis liquid passes over rom the pure water into the solution ; negative in the reverse case of negative osmosis. Now negative osmosis might be simulated in that the nembrane is not semipermeable to the solute. This passes over into the nembrane and so into the pure water ; thereby the volume of the solution s reduced, since a decrease in volume also takes place upon its dilution. Flusin therefore also determined the quantity of electrolyte disappearing rom the solution, and made a corresponding correction. This gives the rue change in volume V_w. Then the quantity Δ is found, that is, the lifference between the amount of water W which the membrane takes up n a certain time in pure water (after careful removal of the substance in he solution of which the membrane had previously swollen) and the mount of water L which the membrane takes up in the same time upon welling in the solution. Hence $\Delta = W - L$; Δ is positive when the nembrane swells more strongly in water than in the solution, negative in he reverse case. We see how V_b (and likewise V_w) and Δ do actually go arallel with one another, and how both show a maximum at a concentraion of 0·33 mol per litre.

Table 183

Comparison of the Swelling and Osmosis Velocities in Osmosis of Water gainst an Aqueous Tartaric Acid Solution through a Membrane of pig's bladder

$t = 16°$

c of Tartaric Acid (molar).	Δ (in c.c.).	V_b (in c.c.).	V_w (in c.c.).
0·17	− 305	− 0·81	− 0·72
0·33	− 341	− 1·13	− 0·88
0·67	− 218	− 1·06	− 0·42
1·33	− 134	− 0·08	+ 0·98
2·00	− 47	+ 0·91	+ 2·65
2·67	0	+ 2·55	+ 4·65
3·33	+ 19	+ 3·53	+ 5·57

The explanation of these phenomena meets with many difficulties. In he first place we must remember that at an earlier point (cf. p. 268) proesses such as negative osmosis were referred to electrokinetic causes ; even in the case of decidedly hydrophilic membranes (collodion containing gelatin). From data at present available it cannot be decided whether ll abnormal osmoses are to be referred to electrokinesis alone, and whether he experiments of Flusin must therefore be interpreted from this point of view, or whether we have to introduce an independent influence of swelling and swelling velocity. It is, however, conceivable that for all hese phenomena, as far as they take place in aqueous solutions, the colloid ion content of the membrane, which after all consists of a protein in the ase of most negative osmoses, conditions the process. This colloid ion ontent might then be decisive both for the electrical charge and hence for the electrokinesis, as also for swelling on account of hydration. One would like to connect the maximum of negative osmosis with a maximum ontent of colloidal protein kations. The reasons given by Pauli [1] in favour

[1] "Kolloidchem. d. Eiweisskörper," p. 45 *et seq.*

of the view that this content passes through a maximum with increase in acid concentration, are not, however, according to J. Loeb,[1] completely justifiable.

The Sol-Gel Transformation

Up to the present we have been mainly considering phenomena in which a gel is formed from a xerogel by the absorption of liquid. It is now our task to investigate the case in which a gel is formed from a sol. A number of examples of this kind have already been discussed; there was no necessity to separate these from flocculation, since this formation of gels completely obeyed the laws of the coagulation of hydrophobic sols; thus, for example, the coagulation of aluminium hydroxide sols (cf. p. 421). The question, it is true, may still be asked: what conditions are required for the separation of the micellæ in flocculi, and for the setting of the whole sol to a jelly? For both in the case of Al_2O_3 sols as with other hydroxide sols (such as those of ferric hydroxide and silicic acid) we observe that flocculi or a jelly are formed according to the conditions of experiment. This behaviour has not yet been investigated in detail, but from some experiments of Fernau and Pauli[2] conclusions can be drawn as to the factors upon which it depends. The first prerequisite for the formation of a gel is sufficient concentration of the micellæ; from dilute sols flocculi always separate. Further, the micellæ must be hydrophilic and remain so upon coagulation. They then bind large quantities of water molecules upon coagulation, or even only envelop them and thus render it possible that finally only ultramicroscopic layers of the dispersion medium separate the coagulated, but still ultramicroscopically small micellæ from one another; that is to say, a gel is formed. Since upon ageing the micellæ of hydroxide sols frequently become more hydrophobic (cf. p. 632), fresh sols of this kind set more easily to gels than old ones. Fernau and Pauli found that a freshly prepared cerium dioxide sol containing about 10 g. per litre was coagulated by electrolytes to a gel; but after the sol had been kept for 10 months at room temperature, it lost this power, and gave a powdery precipitate on addition of electrolytes. Changes had taken place in it similar to those with Fe_2O_3 sols (p. 414).

In the following pages we shall deal with the sol-gel transformation as well known in the case of some lyophilic sols, particularly of solutions of gelatine in water or aqueous glycerine, and of agar in water. This transformation is reversible within certain limits. If, for instance, a gelatine hydrosol of not too low content has been prepared by careful warming (to about 70°), and is then cooled and kept at a lower temperature, it sets to a gel; upon warming it liquefies to a sol, and this process may be repeated many times. It could probably be repeated as often as desired, were it not that an irreversible chemical reaction is continuously taking place in aqueous gelatine sols. This may, for instance, be recognized from the fact that if a gelatine solution be kept at a high temperature, at which it does not gelatinize, the viscosity decreases continuously, until it reaches a considerably lower end value than it had originally.[3] The sol thus formed

[1] *loc. cit.* p. 690.
[2] *loc. cit.* p. 416.
[3] *P. v. Schroeder*, Zeitschr. f. physik. Chemie, **45**, 75 (1903).

has lost the power of gelatinizing.[1] The gelatine thus altered is called β-glutin or also gelatose. Its sol is distinguished by a particularly strong power of emulsifying particles,[2] and acting as protective colloid. Probably this change is a matter of hydrolysis. In gelatine sols with glycerine containing water as dispersion medium, which were thoroughly investigated by Arisz,[3] this hydrolytic change is only distinctly perceptible above 65°. As long as this temperature is not exceeded during the warming of the sol the transformation sol ⇌ gel is actually practically completely reversible. With pure aqueous gelatine sols P. v. Schroeder has tried to diminish the disturbance caused by this process as much as possible by making the previous treatment of the gels exceedingly uniform; for example, he always heated the gelatine solution prepared at 70° to 100° for 5 minutes, and then cooled it to the temperature at which he desired to follow the formation of the gel.

The transition sol ⇌ gel proceeds perfectly continuously. If a temperature-time curve be taken it shows no singular points or rapid changes in direction, as are found, for instance, in the freezing-point curve of a melt. The attempt has been made to follow the transformation thermometrically, by determining "solidifying" and "melting" points, temperatures at which the thermometer dipping in the gel remained fast or began to come loose. These are, however, not characteristic points, although under uniform conditions they allow various sols to be compared.

The viscosity[4] is the property which changes most strikingly during the sol-gel transformation, and hence has been investigated most closely. In the glycerosols of gelatine examined by Arisz the relationships are apparently particularly clear and well defined. If such a sol, which in its preparation has not been heated above 65°, is cooled from a temperature t_1 to a lower temperature t_2 (see Fig. 131), the viscosity (always measured with the Ostwald viscosimeter) follows a curve $a - a'$; the point a does not correspond to any state of equilibrium. If the still liquid sol be then kept at the temperature t_2, the viscosity gradually increases, corresponding to $a' - b'$ (but it must not become so viscous as to be regarded as gelatinized), and finally reaches the equilibrium state b'. If conversely the sol of viscosity b' be rapidly warmed from the temperature t_2 to the temperature t_1, the viscosity moves at first along the curve $b' - b$. When kept at t_1, the viscosity falls from b to the equilibrium value c. These considerations also hold when the viscosity increases to such an extent along the line $a' - b'$ that one speaks of a sol-gel transformation. The critical viscosity at which we assume this transformation to have taken place is represented by the dotted straight line parallel to the axis of abscissæ. The curve $b' - b$ can therefore also refer to a gel, as is the case in Fig. 131. Along the line $b - c$ the sol-gel boundary may be passed over in the reverse sense. Also the equilibrium values of the viscosity, which lie upon the curve $k - k'$, change entirely continuously with the temperature. It may be remarked that approximate measurements have successfully been made of the "vis-

[1] *Liesegang*, Kolloidzeitschr. **2**, 307 (1908). The gold number of a boiled gelatine sol is smaller than that of an unboiled one [*Zsigmondy*, Zeitschr. f. analyt. Chemie, **40**, 714 (1901)].

[2] *loc. cit.* previous note.

[3] *loc. cit.* p. 655.

[4] As regards the viscosity, all the objections raised on p. 639 hold. One must always imagine the word as used in the following description as placed in inverted commas, since with the viscosimeter a viscosity is measured modified by the elastic forces.

cosity" of gels, and it has been shown that the values are continuous with those measured for sols, as Fig. 131 assumes.

We have therefore to deal with equilibria which are set up slowly, the more slowly the lower the temperature. Here, therefore, in the sol-gel transformation for gelatine and similar substances, hysteresis phenomena appear in a particularly pronounced form; while in the case of the swelling-pressure and vapour-pressure isothermals they could be neglected, as was permissible to a first approximation (cf. p. 670), here they completely rule the character of the phenomena. To what striking results hysteresis may lead, may be seen from two examples. When Arisz cooled a gelatine glycerosol, containing 10 per cent. of gelatine, from 70° to 35°, left it at this temperature until it just set, and then warmed it to 44°, it at first became

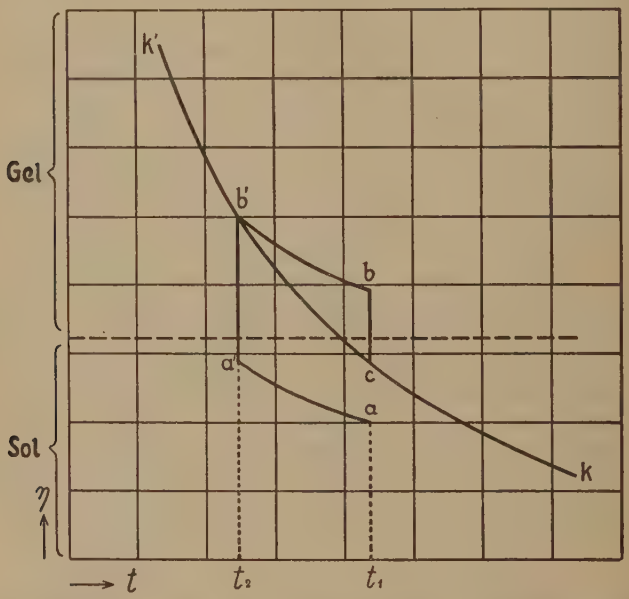


Fig. 131.—Hysteresis of the Sol-gel Transformation of a Gelatine Glycerosol.

liquid again, but after remaining longer at 44° it gelatinized. The curve *defgh* of Fig. 132 makes this behaviour intelligible. If on the other hand the sol remained for two days at 35°, instead of the point *f* the point *f'* was reached; and according to the curve *f'g'h* the gel remained solid even on warming again to 44°. In consequence of the very slow attainment of equilibrium at low temperatures, one can find further examples in which the sol remains liquid at a lower temperature, while with the same concentration it is already solid at a higher temperature. Thus a 1·5 per cent. gelatine glycerosol was solid at 20° after 3 days, while at 2° it was still liquid after 14 days.

From these experiments it appears already that it is difficult to characterize a *tendency to gelatinize*, that is, the free energy with which a sol tends to transform itself into a gel; the methods hitherto employed in this direction give no information concerning equilibria, but only concern-

ing velocities, as, for example, when Lewites[1] determines times of solidification, that is times within which a certain degree of viscosity is reached, for example, the degree which suffices to prevent a sol from flowing out of an inverted test-tube, or when P. v. Schroeder[2] measures the viscosity at regular intervals of time at constant temperature, and uses the increase in viscosity with time $\frac{\Delta\eta}{\Delta t}$ as a measure of the tendency to gelatinize. The method used by Schryver[3] and I. Traube,[4] in which glass balls are allowed to fall in a setting or " melting " gel and the time required for a certain distance of fall determined, may also be mentioned. Whether any conclusions at all concerning the sol-gel equilibrium can be drawn

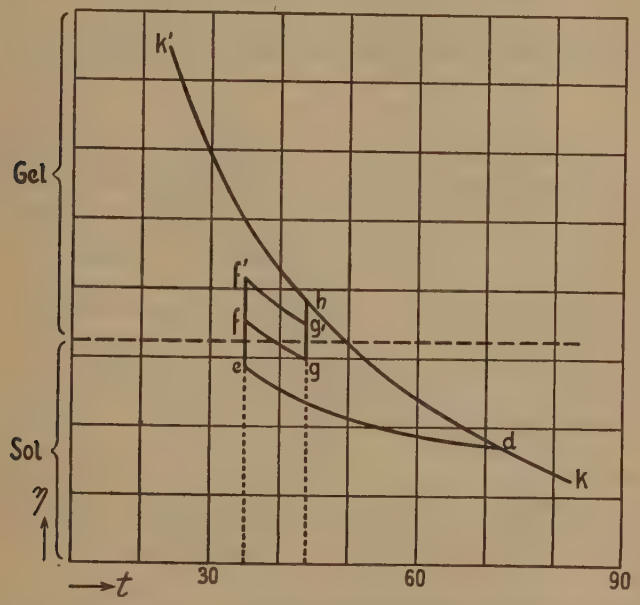


Fig. 132.—Hysteresis in the Sol-gel Transformation of a Gelatine Glycerosol.

from these quantities containing time appears questionable. In any case it must only be done with great caution. It may be remarked that a further consequence of these hysteresis phenomena is, that the solidifying and melting points of a gel above referred to depend upon the rate at which a gel is heated, and that the solidifying-point of a sol lies several degrees below the melting-point of the gel.

The time-course of the increase in viscosity appears to be autocatalytic, as in the case of the coagulation of Al_2O_3, provided that the sol really is transformed into a gel.[5] If with its change in viscosity it remains only in the region of the sol state—at higher temperatures, therefore—an

[1] Kolloidzeitschr. **2**, 161, 208, 237 (1907–8).
[2] *loc. cit.* p. 700.
[3] Proc. Roy. Soc. **87**, B, 366 (1914).
[4] *I. Traube* and *F. Köhler*, Internat. Zeitschr. f. physik. chem. Biologie, **2**, 42, (1915); *I. Traube*, Ber. d. deutsch. chem. Ges. **48**, 938 (1915).
[5] *Arisz*, Kolloidchem. Beihefte **7**, 18 *et seq.* (1915).

initially strong rise in viscosity, which becomes increasingly slower, is observed; that is, an η, t curve concave towards the t axis. An initial concave piece of this kind is also suggested at lower temperatures, in the case of gelatinization, therefore, but it soon bends round into the convex piece of the autocatalytic curve.

A complete continuous change has also been proved in the case of other properties, for example the elasticity of shear (Rohloff and Shinjo [1]) and the Tyndall light (Arisz [2]), during the transition from sol to gel. In a gelatine hydro- or glycerosol at 70° the Tyndall cone is weak. It becomes stronger on cooling, weaker on warming again, and alters continuously in its strength during the sol-gel transformation taking place at constant temperature. Just as the viscosity alters when a quickly cooled or warmed sol is kept at the temperature in question, so also does the Tyndall light. It increases and decreases with the viscosity. Even in sols which are so dilute that no gelatinization is observed, the same changes in the Tyndall light may be followed at constant temperature as in the sol-gel transformation.

The process, therefore, which causes the sol-gel transformation in concentrated solution, takes place in all gelatine sols, even in dilute ones. Both from the macroscopic behaviour of the Tyndall light, as also from the ultramicroscopic experiments of Bachmann discussed earlier (p. 661), we should conclude that the gelatine solution prepared at higher temperatures contains almost exclusively extremely fine particles. This state remains in existence at first at a lower temperature in consequence of the slowness with which the processes take place in these sols, but then gradually passes over into another, in which, doubtless, alongside these small particles much coarser ones—although still amicronic or submicronic—are present. In every case this will be a matter of hydration, and perhaps also of an actual coarsening—in chemical language, of a polymerization. If the solution is sufficiently concentrated, the amount of water bound during this transformation may be so great that the conditions for a gel are given: ultramicroscopic films of dispersion medium between ultramicroscopic particles. As in the case of the stannic acid sols (cf. p. 631) we are dealing here also with equilibria between particles of different orders.

Since we are still without any means of distinguishing between the various kinds of particles present in equilibrium and of determining their quantity, it is intelligible, after all that has been said, that at present we cannot definitely characterize the tendency to gelatinize in its dependence upon other properties of the sol. The following data are therefore only intended to convey an idea of the order of magnitude of these influences. If we first inquire as to the dependence of the tendency to gelatinize upon the disperse phase content we can, in order to characterize it, make use of the viscosity-temperature curve corresponding to a state of equilibrium (curve $k - k'$ in Fig. 131). It rises very steeply with fall of temperature, and this strong curvature in a certain temperature range makes it possible to speak of a solidifying-point, as was already mentioned above; this again corresponds to the appearance of a certain threshold value, when the coefficient in question has large values (cf. p. 321). Extensive measurements of such curves are available for the gelatine glycerosol, and from these it appears that these curves are displaced as the gelatine content increases towards higher temperatures, and that these displacements are large at

[1] *loc. cit.* p. 540.
[2] Kolloidchem. Beihefte **7**, 22 *et seq.* (1915).

small contents, and become continually smaller as the content increases (cf. Fig. 133).

The same is correspondingly true for the solidifying-points. Table 184 contains a few values of this kind, in the first place according to these curves for gelatine glycerosols, and further according to some older results of Pauli and Rona [1] for gelatine hydrosols. Since with small disperse phase content the displacements become greater, contents may be given, at which a sol-gel transformation no longer occurs. Lewites [2] found for a specially purified glutin (according to Moerner [3]), the essential constituent of gelatine, a minimum content of 0·25 per cent., below which the sol no longer solidified at 0°. According to Rohloff and Shinjo,[4] a gelatine sol of 0·18 per cent. no longer shows any tendency to gelatinize. An agar sol with a content as low as 0·1 per cent. solidifies at a temperature of 0°.[5]

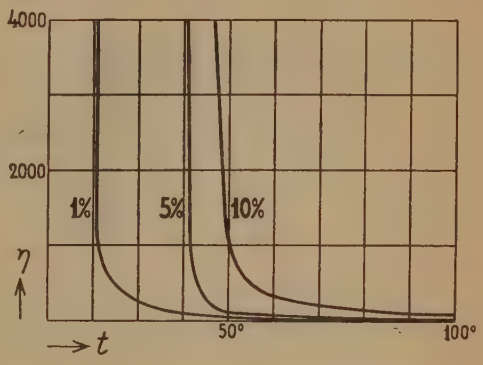


Fig. 133.—η, t Curves for Gelatine Glycerosols of various Strengths.

The glycerosols of gelatine are, according to Arisz,[6] distinctly more viscous than the pure hydrosols and sometimes become solid at a gelatine content and temperature at which the hydrosols remain liquid. This is not true for all concentrations. With small gelatine contents (down to 0·5 per cent.), for example, an aqueous sol may set at 20°, while a glycerosol no longer becomes solid at any temperature.

Particular attention has rightly been paid to the influence of other dissolved substances upon the sol-gel transformation. Pascheles [7]

Table 184

"Solidifying-" and "Melting-Points" of Gelatine Hydro- and Glycerosols with various Gelatine Contents

Sol.	Gelatine Content, per cent.	"Solidifying-point" in degrees.	"Melting-point" in degrees.
Glycerosol	1	20–21	—
„	5	40–41	—
„	10	44–45	—
Hydrosol	5	17·8	26·1
„	10	21	29·6
„	15	25·5	29·4

[1] Beitr. z. chem. Physiol. u. Pathol. **2**, 4 (1902).
[2] Kolloidzeitschr. **2**, 162 (1907).
[3] Zeitschr. f. physiol. Chemie, **28**, 471 (1899).
[4] Physik. Zeitschr. **8**, 442 (1907).
[5] *Lewites, loc. cit.* under [2].
[6] *loc. cit.* p. 655.
[7] Pflüg. Archiv, **71**, 323 (1898).

examined the change in the solidifying-point of gelatine sols in the presence of foreign substances. P. v. Schroeder [1] followed the influence of electrolytes upon the increase in viscosity with time $\frac{\Delta\eta}{\Delta t}$ and compared the difference between these magnitudes in the case of the sol containing salt and the pure aqueous sol

$$\mathfrak{d} = \left(\frac{\Delta\eta}{\Delta t}\right)_L - \left(\frac{\Delta\eta}{\Delta t}\right)_S$$

as characteristic magnitude. Lewites [2] determines the gelatinizing times of gelatine and agar sols for a large number of substances, electrolytes and non-electrolytes. The influence especially of capillary-active substances upon a sodium cholate gel was investigated by Schryver,[3] and by I. Traube [4] that of the same substances, and also of organic dyes upon a gelatine sol. As already mentioned, distinct gelatinization velocities and not equilibria are measured in all cases; a conclusion as to the tendency to gelatinization is therefore uncertain. The influence of $H^{\cdot}$ ions has also perhaps not been sufficiently taken into account, further that the $H^{\cdot}$ ion content quite possibly requires to be kept extremely constant. So much appears to be deducible from these measurements that the lyotropic properties of the salts condition their influence upon gelatinization. The effect is made up additively of that of the single ions. The anions appear particularly prominently in the order

$$SO_4 > \text{acetate} > Cl > NO_3 > Br > I > SCN.$$

Thiocyanates peptize so strongly that in a gelatine sol 0·5 molar for KCNS, no gelatinization, and hence no increase in viscosity, could be observed at 25°.[5] Here we have plainly the effect—and one scarcely caused by a chance change in the $H^{\cdot}$-ion concentration—of the antagonistic behaviour of sulphates, acetates, tartrates, on the one hand, and chlorides, nitrates, bromides, and thiocyanates on the other, which already appeared in swelling processes. The group sulphates, tartrates, etc., favours gelatinization, and therefore raises the solidifying-point, shortens the time of gelatinization, and causes a positive $\mathfrak{d}$. The group of chlorides, etc., act in the opposite sense; they lower the solidifying-point, lengthen the time of gelatinization, and cause a negative $\mathfrak{d}$. P. v. Schroeder found a very complicated dependence of his quantity $\mathfrak{d}$ upon the concentration of the electrolyte, not dissimilar to that observed by Wo. Ostwald [6] in the case of the influence upon the maximum swelling in gelatine gels. The quantity $\mathfrak{d}$ is not, however, definite enough to allow us to expect for it a simple dependence upon concentration, quite apart from the fact that the peptizing influence of the electrolyte has to be taken into account in both cases.

The influence of electrolytes upon the sol-gel transformation must be sharply differentiated from their salting-out action as considered on p. 576. This is evident in large electrolyte concentrations quite independently of whether the salt hinders or favours the sol-gel transformation. Table 185 makes this plain; although KCl depresses the solidifying-point of the gelatine sol, and Na_2SO_4 raises it, with both salts the turbidity which is characteristic of salting-out finally appears.

[1] *loc. cit.* p. 700.
[2] *loc. cit.* p. 703.
[3] *loc. cit.* p. 703.
[4] *loc. cit.* p. 703.
[5] *Freundlich* and *Seal, loc. cit.* p. 57.
[6] *loc. cit.* p. 691.

TABLE 185

Independence of the Influence of Electrolytes upon the Sol-gel Transformation and their Salting-out Power [1]

Electrolyte.	Concentration Equivalents per litre.	Solidifying-point in degrees.
KCl	0·5	19·2
"	1·0	17·4
"	1·5	15·5
"	2·0	12·6
"	2·5	11·1
"	3·0	9·8
"	3·5	8·3
"	4	Turbidity (salting-out)
Na_2SO_4	0·25	23·3
"	0·50	24·9
"	0·75	Turbidity (salting-out)

In the sol-gel transformation as in salting-out—which indeed was regarded as an influence upon the solubility (cf. p. 576)—we are therefore dealing with equilibria, in which water is concerned, but they are two different processes.

The very extensive, but not very detailed experiments of Lewites show that non-electrolytes also influence the time of gelatinization of gelatine and agar sols; the time is shortened by substances such as sugar and polyhydric alcohols, and sometimes greatly lengthened by urea, urethane, especially thio-urea, and other substances. According to Schryver [2] and I. Traube and F. Köhler [3] capillary-inactive substances accelerate gel formation, while capillary-active inhibit it; accordingly an increase in this inhibition takes place according to Traube's rule. With dyes a contrast between basic and acidic appears [4]: acidic lengthen the times of melting of gelatine, and thus act adversely to gel formation; basic favour it.

The behaviour of *soap gels* is similar, although according to present data it is distinctly different in some points; sodium oleate has been chiefly investigated.[5] These gels are transparent elastic jellies, which may be formed from concentrated soap sols. From these we will distinguish as *coagels* the sols and gels containing coagulated soap. We obtain the gel on the one hand by cooling the sol, but also on the other by warming the coagel. In the field of temperature, therefore, the gel stands between sol and coagel and appears to be limited by definite boundaries; a 0·4 molar Na oleate gel could not be obtained below 0°, a 0·4 mol Na oleate coagel not above 23°. At a concentration of 0·6 molar neither a sol nor a gel was observed below + 6°, and no coagel above 25°. Both 0·4 molar and 0·6 molar gels rapidly become liquid at 25°.

As regards a number of properties, sols and gels appeared to be exactly

[1] According to measurements by Pascheles [Pflüg. Archiv, **71**, 336 and 339 (1898)].
[2] *loc. cit.* p. 703.
[3] *loc. cit.* p. 703.
[4] *Traube*, Ber. d. deutsch. chem. Ges. **48**, 938 (1915).
[5] Miss *Laing* and *McBain*, *loc. cit.* p. 658; see also *McBain*, III B.A. Report on Colloid Ch., p. 2.

alike; for instance, as regards refractive index, vapour pressure (measured by the dew-point method, see p. 567), the $Na^{\cdot}$ ion content and the electrical conductivity. Miss Laing and McBain regard solidity and much greater elasticity as the sole differences as compared with the sol; it would be desirable to know whether the Tyndall light is different. The coagels, on the other hand, are totally changed, in the sense that a difficultly soluble neutral soap has separated out. The characteristic form of this separation will be discussed later (p. 724). Hence the conductivity of the coagels is lower, and little different at different concentrations, while that of sols and gels increases rapidly with increase in concentration. In Fig. 134 are plotted the specific conductivities λ of Na oleate sols, gels, and coagels in their dependence upon temperature; curves 1, 2, and 3 refer to 0·2, 0·4 and 0·6 molar gels and sols, while 4, 5 and 6 refer to 0·2, 0·4 and 0·6 molar coagels. Strictly speaking, the coagels of different concentrations should have the same conductivity; for it simply arises from the dissolved soap "left behind" in solution, which in accordance with its solubility stands in equilibrium with the separated soap. The differences depend, according to Miss Laing and McBain, essentially upon the fact that with colloidal separations equilibria are set up so slowly. From a concentrated gel or sol unstable, less hydrated, more soluble soap particles separate than from the dilute; hence the greater conductivity in more concentrated coagels. Along with this must be taken into account the influence exerted upon the conductivity as a result of the space between the electrodes being filled up with soap particles; this influence has not been fully elucidated.

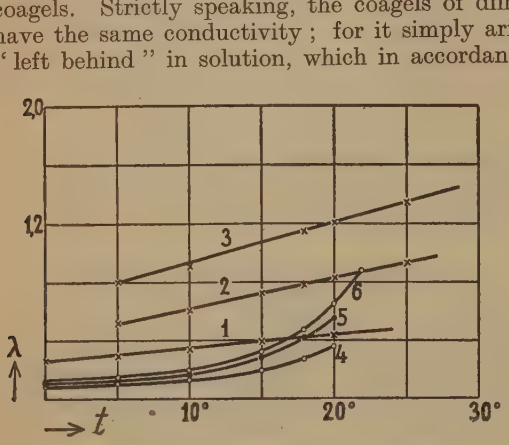


Fig. 134.—λ, t Curves of Sols, Gels and Coagels of Sodium Oleate.

The sol-gel transformation and the formation of coagel in soap solutions are obviously two processes which fully correspond to the sol-gel transformation under the influence of salts and the salting-out of a gelatine sol. It is notable in this connexion that Arrhenius [1] already stated many years ago that the conductivity of a gelatine sol containing salt does not change when it sets to a gel.

Influence of the Degree of Dispersity on the Swelling of a Gel

From the considerations on p. 704 it is probable that gelatine sols and gels are polydisperse, and that the transformations connected therewith take place more and more slowly as the temperature falls. It was already pointed out earlier (p. 686) that this property strongly influences the phenomenon of swelling, not only because the amount of water imbibed and the swelling velocity differ according to the ratio between the numbers of particles of the first and higher orders, but also because the state of a

[1] Oefvers. Stockholm Akad. **6**, 121 (1887).

gelatine gel remains by no means constant under the influence of water; the ratio between the particles is altered, particles of higher orders are split up into those of lower orders. This is especially true of the action of liquid water; not so, or only in a slight degree, of that of water vapour. The following experiments of Arisz [1] speak forcibly in favour of such an interaction between gelatine and water. A 0·5 per cent. gelatine hydrosol prepared at 70° was cooled to 20° and kept at this temperature for 5 days; the viscosity naturally increased distinctly. It was then diluted to half strength with pure water at 20°; the viscosity immediately decreased, but did not remain constant, but sank in the course of several days, tending towards a lower state of equilibrium. If we assume that coarser particles correspond to a higher viscosity of the sol, in which we are justified when we consider that at 70° we find low viscosity combined with weak Tyndall light (see p. 704), this experiment can only be interpreted by assuming that upon diluting with water coarser particles are split up into smaller ones. In perfect agreement with this is the fact that when the solution diluted to half strength is warmed to 70°, and thereby the transformation into particles of lower order made to take place quickly, indeed, driven farther than corresponds to the temperature of 20°, the viscosity upon re-cooling to 20° is much smaller, and now rises towards the same equilibrium value.

Hence if we wish to obtain a gel with particles as coarse as possible, dry gelatine is allowed to swell in water vapour only, while gels with an increasingly larger proportion of finer particles are obtained when a gel thus prepared over water vapour and containing 80 per cent. of gelatine is liquefied at 70°, uniformly mixed with water, and allowed to set at lower temperatures. It is now very surprising [2] that when such gels with decreasing gelatine content are allowed to swell at low temperatures, the gel with the largest content swells most slowly and apparently approaches a quite low maximum swelling, while that containing most water from the start swells far-and-away the most rapidly and strongly. Fig. 135 shows how great these differences are. In it t is the time and a the amount of water imbibed. The experiments were carried out by Hofmeister's method (see p. 689). This is explained according to what has been said above by the gel with the largest proportion of coarse particles swelling much more slowly and imbibing much less water than the gels containing increasingly larger proportions of finer particles. Arisz had carried out these experiments with plates 4 mm. thick. When he took finer ones—about 1 to 0·5 mm. thick but of equal, fairly high (50 per cent.) gelatine content—not only was the S.V. large, but also the maximum towards which the plate apparently tends, lies higher, the smaller the thickness; simply because with the rapid and intimate action of water on these finer pieces the splitting-up of the particles of higher order into smaller ones takes

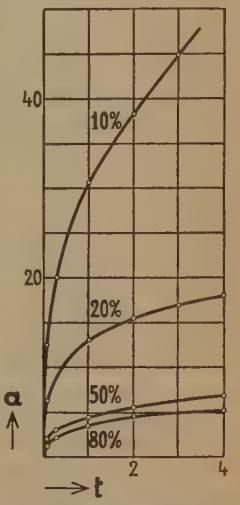


Fig. 135.—Dependence of the Swelling of a Gelatine Gel upon the Gelatine Content.

[1] Kolloidchem. Beihefte **7**, 42 *et seq.* (1915).
[2] *Arisz*, Kolloidchem. Beihefte, **7**, 51 *et seq.* (1915).

place more quickly, and these not only bind more water but do so more rapidly.

All experience goes to show that in a gelatine gel, independently of its state of swelling, equilibria are set up between the particles of different sizes, which greatly alter the swelling velocity and the (apparent) maximum swelling. The further fact may be mentioned that when swollen gels are allowed to age, the power of swelling decreases on account of the coarsening of the particles. Exceedingly complicated relations appear when gels are allowed to age at a temperature other than that at which they have swollen. Here the reader must be referred for details to the work of Arisz. Under certain circumstances it is observed that a gel which has swollen at 10° when warmed to 20° at first shrinks before it again rapidly swells; this is perhaps an expression of the fact to be expected, that in accordance with the heat of swelling, if the state of the gel remains exactly the same, the maximum swelling should decrease with rise of temperature.

The fact that these polydisperse equilibria are more rapidly set up with liquid water than with water vapour, and that they strongly affect swelling, has doubtless a share, as briefly remarked above (p. 672), in the phenomenon described as the Schroeder paradox, which has been discussed in detail earlier.

When we consider that all these influences take a share in the swelling of gelatine in aqueous electrolyte solutions, the complicated curves as described by Wo. Ostwald (p. 691) become intelligible. We ought indeed to first decide in the case of swelling how far electrolytes shift the polydisperse equilibrium, and how far the actual swelling equilibrium. There is a certain possibility of separating the two cases, for the influence of electrolyte upon the sol-gel transformation perhaps affects to a large degree only the polydisperse equilibrium. It is true that by the methods of measurement hitherto employed, it is essentially the velocity of attainment of these equilibria that has been determined. It is possible that the similarity of the swelling curves observed by Wo. Ostwald in various electrolyte solutions with the Schroeder curves for the increase in viscosity during the sol-gel transformation in the same solutions (see p. 706) depends only upon the shift in the polydisperse equilibrium, the resulting swelling being measured in the swelling experiments, and not the swelling of strictly comparable gelatine gels of like inner structure.

In the case of caoutchouc gels with organic liquids the equilibria appear to be set up more smoothly according to E. Posnjak's [1] experiments; but in their case also, according to F. Kirchhof,[2] there is a decided difference between swelling in the liquid and in the vapour; in the vapour the S.V. is much smaller, the maximum swelling apparently reached is lower. It would therefore appear as if here also the particles of higher order are more quickly split up into those of lower order by the liquid than by the vapour.

The same difference between the reaction velocity of liquid and vapour is not without other examples; thus purpureo-chromic chloride is formed violently by the action of liquid ammonia upon violet chromic chloride, while with gaseous ammonia the reaction only takes place to quite a slight extent.[3]

[1] *loc. cit.* p. 673.
[2] *loc. cit.* p. 696.
[3] *Christensen*, Zeitschr. f. anorg. Chemie, **4**, 229 *et seq.* (1893).

The Production of Gels from Coarsely Crystalline Substances

Gels are most frequently formed by the swelling or solution of a coagel and by the sol-gel transformation. But structures which one will probably recognize as gels are sometimes also formed in the following manner. Coarsely crystalline substances can be so changed by chemical action that finally only a gel-like skeleton remains behind. An example of this kind is observed in the preparation of Al_2O_3 sols (cf. p. 520). A crystalline precipitate of basic aluminium acetate is first prepared by heating an acetic acid solution of aluminium acetate. If this precipitate is frequently washed with distilled water, it is gradually changed into a sticky amorphous mass, which might be regarded as a gel, and this finally peptizes in water. By removal of acetic acid, therefore, $Al(OH)_3$ has been left behind, the atoms of which under these circumstances have not apparently the power of arranging themselves in a coarsely crystalline space lattice, but form a finely crystalline or amorphous mass.

It is said of many silicates, for instance, gadolinite,[1] that they are changed into jellies by the action of acids. It is true that here, as in all these cases, it is not easy to decide whether after all a sol is not first formed, which only gelatinizes very quickly ; in the case of silicic acid, which may also sometimes appear in a soluble form (see p. 626), this possibility more readily suggests itself than in the case of the difficultly soluble aluminium hydroxide.

These processes play a certain part in mineralogical and geological questions. Many minerals which one is inclined to regard as gels have perhaps not been formed as coagels from sols, but in this way directly by chemical action upon crystalline minerals. Since Cornu [2] pointed out the importance of gels in the mineral kingdom, a systematic investigation on a larger scale does not yet appear to have been carried out as to whether minerals regarded as gels on account of their external characteristics are so in reality. Radiospectroscopy would first of all allow of a decision whether they are amorphous or crystalline, tests of the adsorptive power towards dyes would supplement these results, and give information concerning the question of the electric charge, possible exchange adsorption, and so on. It is probable, in view of the long spaces of time with which geologists have to reckon, that one will chiefly observe structures which have been formed from gels by slow crystallization. The observation of Cornu, that gels and crystals of like composition are often met with, already belongs here.

The many kinds of surface soils, which are in part inorganic, in part organic gel-like matter, constitute a particular case of this mineralogical colloid chemistry. Here the investigations of P. Ehrenberg [3] have especially enriched our knowledge.

Some Special Cases of Gel Formation

As appears from the behaviour of soap gels, gels may form intermediate stages between a sol and a coagel, which latter, in its final state of equili-

[1] See *Klockmann*, "Lehrbuch der Mineralogie," 5th to 6th Ed., Stuttgart, 1912, p. 551.

[2] Particularly a series of papers in the Kolloidzeitschr. **4** (1909). Concerning pronouncedly jelly-like gels containing SiO_2 and Al_2O_3 see e.g. *Weissenberger*, Kolloidzeitschr. **27**, 69 (1920).

[3] "Die Bodenkolloide," Dresden and Leipzig, 1915.

brium, will be more or less coarsely crystalline. It would appear as if in many processes gels are formed as intermediate stages, even in cases where this has not at first been expected. Thus much tells in favour of the view that their temporary formation must be taken into account to a considerable extent in the case of *hydraulic cements*. We may agree with those who hold the opinion,[1] that the equilibria elucidated on the basis of the phase rule do not give us any information as to why the polyphasic system finally formed has hydraulic properties, why, therefore, it sticks together firmly in a coherent mass; the same phase equilibrium might hold if we were only dealing with a loose heap of crystals. Hermann Ambronn [2] was able to show microscopically and ultramicroscopically that a gel is formed during the hardening of Portland cement; this binds the cement clinker particles together; it is further interspersed with fine crystalline needles, and so the hard coherent mass finally results. According to further investigations, such as those of W. Michaelis,[3] Keisermann [4] and others, we must form the following picture of the setting of cement. The cement clinker burnt at a high temperature contains calcium silicate and aluminate, which at ordinary temperatures are not stable towards water. They are attacked, hydrated, and change into other compounds; thereby the gel mentioned, with the needle crystals, which determine the strength and hardness of the set cement, interspersed in it, appears. According to Keisermann,[5] the gel and the needles, upon which the setting depends, consist of monocalcium silicate; the aluminate is only important because it reduces the melting-point and shortens the time of hydration. He investigated systematically the different powers of adsorbing dyes possessed by the solid phases appearing in these processes, whereby the contrast between positive and negative adsorbents in their behaviour towards acid and basic dyes proved to be valuable; aluminate could be stained by patent blue (an acid dye) in alkaline solution, but not the negative silicic acid and silicates; the silicic acid, on the other hand, with methylene blue; the silicates with methylene blue in acetic acid solution, by which the silicic acid was set free; lime was detected by alcoholic anthrapurpurin solution.

It is probable that the setting of *plaster of Paris* depends upon similar processes. Here also the statement that the hemihydrate passes over into the stable dihydrate does not suffice to explain why the mass becomes hard and coherent. This would be intelligible on the assumption that the dihydrate separates as a gel from supersaturated solution, and that from this gel a closely felted coagel of crystalline dihydrate is then formed. The observations of Wo. Ostwald and Wolski [6] may be interpreted throughout in favour of the occurrence of a process of this kind. If the course of setting is followed with the viscosimeter, the curves showing the dependence of the time of efflux upon the time have an autocatalytic form, such as is known in the case of related colloido-chemical processes (gelatinization of sols, reversal of adsorption, and others); also the dependence of the course of the curves upon the proportions of water and plaster and

[1] See *Wo. Ostwald* and *Wolski*, Kolloidzeitschr. **27**, 78 (1920).
[2] Tonindustriezeit. **33**, 270 (1909).
[3] Kolloidzeitschr. **5**, 9 (1909).
[4] Kolloidchem. Beihefte **1**, 423 (1910).
[5] But see also *W. Michaelis*, Kolloidzeitschr. **7**, 320 (1910).
[6] *loc. cit.* under [1]; further particularly *Cavazzi*, Kolloidzeitschr. **12**, 196 (1913); *I. Traube, ibid.* **25**, 62 (1919).

upon the fineness of the latter are in agreement with this view.[1] A gel formation which may perhaps be taken as typical of many other colloido-chemical processes is the transformation of *styrol* into *metastyrol*. According to Stobbe and G. Posnjak[2] styrol ($C_6H_5CH = CH_2$) is changed by warmth and light into a mass which may be either glass- or jelly-like. This is to be regarded as a gel, the micellæ of which consist of metastyrol, a polymeric hydrocarbon, which, however, in contrast to styrol is not unsaturated and changes on distillation into styrol again. More or less styrol is contained in the gel as gel liquid. Here also viscosimetric measurements show that the course of the reaction on illumination is autocatalytic.[3]

Stobbe and Posnjak already point out that caoutchouc probably belongs to this group of gels. The substance which later becomes caoutchouc may be extracted from the milky juice of rubber-producing plants as a mobile oil. This polymerizes under the influence of light, moisture, and acids to caoutchouc, a gel which doubtless consists, like that of metastyrol, of micellæ of a highly polymerized compound (probably a polymeride of dimethylcyclooctadiene) together with a residuum of the original or of a less polymerized liquid compound. We cannot here go into the colloidal chemistry of caoutchouc, which has been already worked upon in great detail.[4] It may only be remarked here that the original rubber-milk, like animal milk, largely resembles a hydrophobic sol protected by protein, and that the taking-up of sulphur during vulcanization is perhaps to be regarded as an adsorption in its early stages.

With a series of gels of organic substances the fact pointed out in connexion with soap gels (p. 707), that they appear as unstable intermediate stages, is again met with. In course of time they change, like the coagel of soap, into crystalline masses together with the saturated solution. Hatschek[5] examined the gel of *camphorylphenylthiosemicarbazide*. Its alcoholic solution, when rapidly cooled, sets to a gel, from which is formed at room temperature first a gel interspersed with crystals together with a little liquid, and finally a crystalline mass under the saturated solution, which is no longer gel-like. With contents over 5 per cent. the gel was observed as an intermediate state which was stable only for a few seconds or minutes. The 5-*dimethylaminoanilo*-3-4-*diphenylcyclopentene*-1-2-*dione* described by Hardy[6] behaves similarly. Here a whole series of liquids form suitable dispersion media. The gels have their various degrees of stability: the ethyl ether gel one of only minutes; the gels with carbon tetrachloride, water-ethyl alcohol and water-acetaldehyde keep for days. Finally crystals are formed together with the saturated limpid solution. At higher temperatures the gel may again be liquefied to a sol. An aqueous gel was obtained by Doehle and Rassow[7] by mixing a solution of the calcium salt of the sulphonic acid of *benzothiazolemethane sulphide* with a solution of corrosive sublimate. The micellæ formed probably consist of the normal

[1] Attention may also be drawn to the investigations of *Kohlschütter* and *G. Walther* [Zeitschr. f. Elektrochemie, **25**, 159 (1919)] concerning the behaviour of lime-water mixtures.

[2] Lieb. Ann. **371**, 259 (1909).

[3] The similarity with many other gelatinization processes may here naturally be superficial; a purely chemical change also takes place.

[4] See e.g. *Wo. Ostwald*, "Die Welt der vernachlässigten Dimensionen," p. 173 *et seq.*

[5] Kolloidzeitschr. **11**, 158 (1912).

[6] Proc. Roy. Soc. **87**, A, 29 (1912).

[7] Kolloidzeitschr. **12**, 71 (1913).

Hg salt of this acid; from this sol a basic Hg salt separates in course of time. The jellies given by some *cotton dyes*, such as cotton red, chrysophenin, and others, in aqueous solution, have been investigated by Haller.[1] It is physiologically important that aqueous solutions of *uric acid salts*, especially those of lithium urate, when prepared in the warm, set first of all in jelly-form on cooling; the jellies gradually change into a crystalline paste.[2]

The reader may be reminded here that *smokeless powders* are gels consisting of nitrocellulose suitably nitrated and gelatinized with organic liquids; as gelatinizing liquids alcohol-ethyl ether, acetic ester, and others, and lately also nitroglycerine are employed. Various additions, such as camphor, diphenylamine, etc., serve to lower the rate of decomposition, which makes the too violent explosives unsuited for ballistic purposes, and to increase the stability; for these nitro-compounds tend to an autocatalytic decomposition.

The Density of Gels

As already frequently pointed out (p. 673), a decrease in volume takes place upon swelling; the swollen gel has a smaller specific volume than is calculated additively from the specific volumes of xerogel and imbibed liquid. This was first shown by Lüdeking [3] for gelatine gels, and closely investigated by Rodewald [4] on starch grains; a series of further measurements are due to Katz.[5] Also upon the swelling of caoutchouc in organic liquids this reduction in volume is observed.[6] It is measured by determining the density of the dry and swollen gel by means of a pyknometer; with gels which imbibe water petroleum ether is suitable for filling the pyknometer. The volume contraction C signifies in the following pages the change in volume in cubic centimetres when one gram of dry gel imbibes a grams (or millimols as the case may be) of liquid, the difference, therefore, between the observed and calculated volumes. Table 186 shows how, in the case of casein, C changes with the water content of the gel. The reduction in volume is thus relatively largest with the first amount of water imbibed; it therefore behaves similarly to the heat of swelling. It thus comes about[7] that it may also be expressed by the same formula as the latter (see formula (1), p. 680):

$$C = \frac{\gamma a}{\delta + a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

How far the agreement extends is shown by Table 186, in which the constants γ and δ refer to the a values in grams. C and Q are actually approximately proportional to one another, and the volume ratio $\frac{C}{Q}$ little different for various gels imbibing water. This connexion is intelligible since heat evolution and contraction are both expressions of the attraction between xerogel and liquid.

[1] Kolloidzeitschr. **22**, 49 (1918).
[2] See especially *Schade* and *Boden, loc. cit.* p. 634.
[3] Wied. Ann. **35**, 552 (1888).
[4] Zeitschr. f. physik. Chemie, **24**, 193 (1897).
[5] Kolloidchem. Beihefte **9**, 70 *et seq.* (1917).
[6] *E. Posnjak,* Kolloidchem. Beihefte **3**, 431 (1912).
[7] *Katz, loc. cit.* under [5].

TABLE 186

Volume Contraction when Casein imbibes Water

$\gamma = 0{\cdot}088$; $\delta = 0{\cdot}229$.

(Amount of Water taken up by 1 gram dry Casein) in grams.	millimols.	C (obs.).	C (calc.).
0	0	0	0
0·0269	1·49	0·0077	0·0092
0·0806	4·47	0·0217	0·0229
0·1207	6·695	0·0317	0·0304
0·1661	9·22	0·0379	0·0370
0·2139	11·87	0·0414	0·0425

THE HEAT EXPANSION OF GELS

The thermal coefficient of cubical expansion of a gel usually differs little from that of the liquid imbibed. Thus v. Bjerkén[1] found for a glycerogel of gelatine between 13° and 32° a value of 0·00047, while the glycerine from which the gel had been prepared had a value of 0·00046 between 11° and 40°. Hence the influence of the more strongly expanding liquid preponderates.

A curious behaviour as regards thermal expansion is shown by many gels in a stretched condition. It was first observed on india-rubber.[2] If a thin band of raw rubber be quickly stretched to a multiple of its original length, it heats up so strongly that it can be felt to be warm in the middle. If it be suddenly cooled in this hot stretched state by cold water, it does not immediately return to its original length on being released, as it would do if it had not been suddenly cooled ; on the contrary it retains at first the length produced by stretching, and only regains its original state after a series of peculiar twistings.

As opposed to what is usual, the stretched rubber therefore liberates heat upon further stretching. It is then required by thermodynamics that a stretched rubber band should contract upon warming, and expand upon cooling. This is the case when heating and cooling take place rapidly.[3]

A similar behaviour is shown by glue jellies according to v. Bjerkén's experiments (*loc. cit.*). Stretched in the form of a band between two glass tubes, it contracted upon warming and expanded again on cooling, and accordingly warming was observed on stretching, and cooling on contraction. In this case the important fact was also demonstrated that the gel state is a necessary condition for this phenomenon. The peculiar behaviour could not be observed with the dry glue. This cooled itself on expansion. These peculiarities of the thermal expansion are difficult to represent numerically, since hysteresis phenomena play a large part.

It appears to me that these phenomena essentially depend upon the equilibria between particles of higher and lower orders, the existence of which in these gels we have good grounds to assume. If such a gel is very strongly stretched, particles of a higher order are torn into particles of a

[1] Wied. Ann. **43**, 817 (1891).
[2] Particularly *Joule*, Phil. Trans. **149**, 101 (1859).
[3] *v. Bjerkén, loc. cit.* under [1].

lower order. New interfaces are thereby formed, the liquid contained in the gel—even in raw rubber we must assume, in view of the similarity with glue gels, a certain amount of imbibed liquid (see also p. 713)—wets this interface, and heat is developed in consequence of the heat of swelling. That it can be so considerable in amount doubtless arises from the fact that the amount of heat developed upon imbibition is very large precisely for the first quantities of liquid taken up (see p. 681). If the stretched gel is cooled suddenly, as in the experiments on rubber above described, it is brought into a region of temperature in which the transformation of particles from lower to higher orders does not take place so rapidly; hence the gradual return to the old state may be followed. If a stretched gel is quickly warmed, a certain shrinkage will take place,[1] and upon cooling a corresponding swelling; while with slow warming the shift in the equilibrium between the particles of various orders under the influence of the imbibed liquid (see p. 708) preponderates, and the behaviour alters. These phenomena will first be definitely elucidated when the equilibria between the particles of various orders are better known, and especially when the swelling of stretched gels has been more closely investigated.

It deserves remark that stretched muscles show a similar departure from regular behaviour as regards thermal expansion.[2]

The Elastic Properties of Gels

In their elastic properties the gels resemble solids to a large extent.[3] Also in their case the considerable number of constants which characterize elasticity must be taken into account. The theory of the elasticity of gels also has a special character, in that many of them, such as rubber, show very striking elastic properties. This is not the place to examine these relationships in detail[4]: only a few elastic properties will be considered in relation to the degree of swelling, and attention drawn to the degree to which these mechanical properties promise information concerning the structure of the gels.

Three elastic constants will first be considered: the *bulk modulus* β—the ratio of the relative change in volume to the change in pressure when the latter is applied on all sides—*Young's modulus* E_D—the ratio between load and relative elongation in the case of longitudinal extensions—and Poisson's ratio μ—the ratio of the relative lateral contraction to the relative change of length when the extension is in one direction. The theory of elasticity gives the following relation between the three quantities

$$E_D = \frac{3(1 - 2\mu)}{\beta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The *compressibility* of gels has been but little investigated; the most detailed measurements are those of Barus[5] on gelatine gels. His arrangement was as follows. The gel was contained in a capillary tube, in contact

[1] *Arisz* (cf. p. 710), also observed shrinkage upon rapid warming.

[2] *Schmulewitsch*, Wien. Medizin. Jahrb. **15**, 3 (1868); *Samkowy*, Pflüg. Archiv. **4**, 399 (1874); *Blix*, Zeitschr. f. Biolog. **21**, 190 (1885).

[3] Thus silicic acid gels contained in test tubes give when the tube is struck a definite musical tone which varies with the properties of the gel [*H. N. Holmes, W. E. Kaufmann* and *Nicholas*, Journ. Amer. Chem. Soc. **41**, 1329 (1919)].

[4] See among others *Villari*, Pogg. Ann. **143**, 88 (1871); *Röntgen, ibid.* **159**, 601 (1876); *Russner*, Wied. Ann. **43**, 533 (1891); *Lundal, ibid.* **66**, 741 (1898); *O. Frank*, Ann. d. Physik (4), **21**, 602 (1906).

[5] Amer. Journ. Science, **6**, 285 (1898); Science, **8**, 681 (1898).

above with a fixed thread of mercury, and below with a thread of mercury connected to a hydraulic pump which transmitted the pressure. The movement of the lower meniscus with known pressure allows the calculation of the bulk modulus. With moderate pressure the compressibility of gelatine gels was fairly large at room temperature, $\beta = 10 \times 10^{-6}$; with solids the order of magnitude of β is usually about 10^{-6}. When the temperature rose and the gel was transformed into a sol, β also increased and reached a value of 48×10^{-6}, practically equal to that of water.

We are better informed concerning Young's modulus. It is found by stretching a cylinder or strip of the gel by means of a weight P suspended from it, and determining the elongation Δ. If the length of the cylinder is l, and its diameter $2r$, then with not too great an elongation the change in length is proportional to the length and weight, and inversely proportional to the cross-section, and the proportionality factor is the reciprocal of Young's modulus, since the more elastic the body the smaller the extension; hence

$$E_D = \frac{P}{\pi r^2} \frac{l}{\Delta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Young's modulus depends greatly upon the degree of swelling; it increases, according to Leick's [1] measurements on gelatine gels, and Reinke's [2] on Laminaria discs, quadratically with increase in disperse phase content c; thus

$$E_D = kc^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

How far this is true, is shown by Table 187.

TABLE 187

Dependence of Young's Modulus upon the Degree of Swelling of Gelatine Gels

c (in per cent.).	E_D (kg./sq. mm. $\times 10^3$).	$k \times 10^5$.
10·0	2·42	2·4
10·2	2·66	2·6
18·6	9·78	2·8
18·9	9·77	2·7
30·0	15·45	1·7
32·0	21·57	2·1
45·0	29·44	1·5

With small disperse phase contents, and hence high degrees of swelling, E_D becomes very small, and finally zero.

Since, as just described, β changes only within small limits in the transition from gel to sol, it follows from equation (1) that the great decrease in E_D can only be combined with a corresponding change in μ, as Katz [3] has pointed out. According to the theory of elasticity, μ, the ratio of the relative lateral contraction to the relative change in length, is equal to $\frac{1}{2}$ for small extensions when the total volume does not change. This is the case with a liquid, the molecules of which are freely movable, with which

[1] Ann. d. Physik (4), **14**, 139 (1904). [2] *loc. cit.* p. 673.
[3] Kolloidchem. Beihefte **9**, 151 (1917).

therefore the lateral contraction is able to follow the change in length to such an extent that the volume remains unaltered. According to equation (1), however, when $\mu = \frac{1}{2}$, Young's modulus is zero, which is also true for a liquid. If E_D becomes very small, as for highly swollen gels, μ approaches the value $\frac{1}{2}$ more and more. According to experiments by Maurer [1] on gelatine gels, μ could not actually be distinguished from this value. v. Bjerkén [2] was further able to show that even with great elongations, at which μ is no longer equal to $\frac{1}{2}$, the volume of a gelatine jelly is practically unaltered. It is to be expected that with low degrees of swelling μ will depart more and more from $\frac{1}{2}$. Since β is very small, small departures of μ from the value $\frac{1}{2}$ (thousandths and less) suffice according to formula (1) to give the values of Young's modulus observed with gels. With solids, such as metals, μ has values as low as 0·2.

As regards Poisson's ratio μ, gels very largely resemble a liquid, the resemblance being greater the more liquid they contain. Therewith two other properties are in agreement.[3] The *tensile strength* of gels is comparatively small and decreases greatly with swelling, while their *flexibility* is great and increases with swelling; as measure of flexibility we take the elongation at which the gel is torn apart. It is true that extensive series of experiments on well-defined gels are not available. But Reinke found that with Laminaria the force necessary to tear it apart sinks to $\frac{1}{10}$ when 350 per cent. by volume of water has been imbibed. Similar results were given by experiments of W. Herzberg [4] on paper containing various quantities of water; here also it was shown that the breaking strain increases with the water content. It is also known of caoutchouc that its tensile strength is small, its breaking strain great. The limiting value of the tensile strength which a gel swollen with water would approach, would therefore be the tensile strength of the water itself, as observed in the experiments described on p. 10 (order of magnitude 50 to 100 atmospheres per sq. cm.). The breaking strain of a swollen gel is, however, great, since a liquid can easily change its shape and follow the tension without changing its volume.

The equilibria between the particles of various orders, which have already been used to explain the peculiarities of thermal expansion, will also greatly influence the elastic properties. This is already proved by the fact that, according to Fraas,[5] Young's modulus for gelatine gels obtained by allowing sols to set, increases greatly immediately after preparation, and at room temperature only approaches a definite, well-defined value after 24 hours. This time-change is again very much dependent upon the previous history of the gel.

It is therefore possible that the influence of electrolytes and other foreign substances upon the elastic properties of gelatine gels is connected with the power of these substances of displacing the aforesaid equilibria between particles of different orders. As a matter of fact, a connexion between the change in Young's modulus of gelatine gels due to foreign substances and their influence upon the sol-gel transformation is unmistakable. Thus according to Leick [6] chlorides and nitrates decrease the Young's modulus of gelatine gels, and correspondingly adversely affect gel

[1] Wied. Ann. **28,** 628 (1886).
[2] *loc. cit.* p. 715.
[3] See *Katz,* Kolloidchem. Beihefte **9,** 151 *et seq.* (1917).
[4] "Papierprüfung," Berlin, 1902, p. 9.
[5] Wied. Ann. **53,** 1082 (1894).
[6] *loc. cit.* p. 717.

formation (see p. 706), while sodium sulphate and cane sugar increase Young's modulus and favour gel formation.

If it be true that these equilibria are of importance for the theory of the elasticity of gels, a general theory of the elasticity that did not go into the number and size of these micellæ would hardly make much progress. Hence we shall not go further into Reiger's [1] application of the Maxwell theory of the elasticity of liquids, which only appears applicable to viscous liquids,[2] to gels. According to this the viscosity of the gel is connected with the simple rigidity, and with the relaxation time, the viscosity being equal to the product of these two quantities. The relaxation time is the time necessary for the internal elastic strain to fall to $\frac{1}{e}$ of its original amount. One might hope to measure it in gels by following the time-change of the double refraction caused by the strain in the gel. But this optically measured relaxation time does not appear to agree with the one concerned in the mechanical processes.[3] The simple rigidity E_S is connected with the extension by the equation

$$E_S = \frac{E_D}{2(1 + \mu)}.$$

The whole elastic behaviour of gels is dominated by the facts that on the one hand cohesion and elasticity are present as with ordinary solids, on the other hand that the numerical preponderance of liquid molecules generally present allows the properties of the liquid to appear so strongly that the gels behave like solid liquids. How greatly the liquid molecules preponderate is brought home to one by considering that at room temperature a 1 to 2 per cent. gelatine gel is still solid (see p. 705). Assuming a molecular weight for gelatine of 10,000 onwards—one might also very well assume 50,000 as for albumin (cf. p. 557)—we have about 27,000 water molecules to 1 gelatine molecule in a 2 per cent. gel. That the properties of the water are prominent is less surprising than that so small a number of gelatine molecules holds the gel together. We must naturally hereby take into account that a large part of the water molecules builds up the micellæ together with the gelatine molecules, and that therefore the number of molecules of water which serve as intermicellar liquid is smaller.

The small amount of a gel-forming substance that is required in many cases for gel formation appears to me a further circumstance in favour of the view that the radius of molecular action does frequently extend beyond one layer of molecules (see p. 315). If, in the example just given, we assume the gelatine molecule to be in the interior of a cube, surrounded by the 27,000 water molecules, the gelatine molecules would be about 6 $\mu\mu$ distant from one another. Now this number can be very much altered if these molecules are not spherical, but somewhat elongated, and if a large number of water molecules actually belong to the gelatine micella. In any case, however, we come to distances which are larger than the diameter of a medium-sized or small molecule.

A curious phenomenon in which the solid-liquid nature of gels is very pronounced has been described by Barus.[4] When in the compressibility

[1] Physik. Zeitschr. **2**, 213 (1901).

[2] *Reiger*, Ann. d. Physik (4), **31**, 51 (1910); see also *Faust* and *Tammann*, Zeitschr. f. physik. Chemie, **71**, 51 (1910).

[3] *Reiger*, Ann. d. Physik (4), **31**, 93 (1910).

[4] *loc. cit.* p. 716.

measurements mentioned above (p. 716) he increased the pressure very considerably, the lower mercury meniscus took on a conical pointed form, and then a minute globule of mercury was suddenly shot off the point, and penetrated 10 to 20 cm. into the gel; the initial velocity amounted to several metres per second, but decreased rapidly; the diameter of the globule was less than $_1\!/_{\!0}$ mm. This process was several times repeated at constant pressure.

The explanation given by Barus, somewhat modified, is as follows. The gel first behaves like a solid and has a certain resistance. If the pressure is increased, the mercury is forced into a capillary space, and the point there exerts a very high pressure, so that finally the structure of the gel collapses in front of the point and the micellæ are forced sideways. In the sudden release of pressure thus caused a mercury drop is torn off, which is now hurled into the gel; for between it and the mercury meniscus transmitting the pressure there is at first only liquid, which passes on the pressure. But the gel torn locally sets again to a solid, especially in view of the fact that increased pressure must favour gelatinization (see p. 685), and the series of phenomena can commence anew.

The Optical Properties of Gels

Of these the double refraction has the place of first importance; it may occur under various circumstances and has been frequently referred to. We can here in the case of gels (and xerogels) clearly distinguish between the various possibilities, which in other cases are not easy to separate.

In the case of sols (p. 410) we are confronted with the question whether stream-double refraction depends upon a rod double refraction or upon a double refraction of the micellæ themselves. Also in the case of gels these two possibilities may be distinguished. A *rod double refraction* may be present because structural units in themselves isotropic are arranged in an anisotropic manner; or further, we may have *double refraction due to the similar orientation of anisotropic particles.* This double refraction may be present in the gel from the start, or it may be first produced by pressure or tension, because under this influence the particles are arranged in a certain position relative to the directions of pressure or tension. The stream double refraction of sols belongs entirely to the category of double refraction due to the similar orientation of anisotropic particles. With gels a third possibility appears—*double refraction due to tension and compression* in the true sense; with this the change in density produced by tension and compression in an isotropic solid not containing particles having a double refraction of their own suffices to produce double refraction, as with the double refraction of glass or regular crystals under tension and compression.

A *rod double refraction* is readily distinguished from the two other possibilities. If we have a xerogel with micellæ of refractive index n surrounded by a liquid of refractive index n_2, then according to O. Wiener's theory, the relation

$$n_o^2 - n_a^2 = -\frac{\varphi_1\varphi_2(n_1^2 - n_2^2)^2}{\varphi_1 n_2^2 + \varphi_2 n_1^2 + n_2^2}. \quad . \quad . \quad . \quad . \quad . \quad (1$$

holds. Here φ_1, φ_2 are the ratios of the volumes of micellæ and liquid to the total volume, n_o and n_a the indices of refraction of the ordinary and extra

[1] Ber. d. Sächs. Ges. d. Wiss. **61,** 113 (1909); Abhandl. d. Sächs. Ges. d. Wiss. **32,** No. 6 (1912).

ordinary ray in the body composed of xerogel and liquid. The expression on the right of (1) is always negative, the rod double refraction therefore always positive. It becomes zero when the micellæ and the surrounding liquid have the same refractive indices. If therefore the double refraction changes with the liquid in which the particles are immersed, a rod double refraction is present. If it disappears when the liquid is suitably chosen, we have a pure rod double refraction.

A clear case of this kind was found by Hermann Ambronn [1] for fibrous alumina. Its double refraction is only strong in air ; it is weak in alcohol and monobromnaphthaline and hardly detectable in Canada balsam. The lattice-like structure of this xerogel is not microscopically recognizable, it must be ultramicroscopic. Certain diatom shells behave similarly according to older experiments of H. Schultze,[2] which Ambronn was able to confirm ; here a regular lamellar structure can be proved microscopically.

The two other cases of double refraction, that due to orientation of anisotropic particles, and that to tension and compression, cannot at present be distinguished in the case of gels. With sols this was less difficult. There is no doubt that stream double refraction, which can be produced by such gentle mechanical treatment, depends upon the orientation of anisotropic particles, provided that the characteristics of rod double refraction are absent. This is however the case, since stream double refraction is by no means always positive, as required by theory for rod double refraction, but often negative ; and this negative stream double refraction depends upon a negative double refraction of rod-shaped micellæ or a positive one of disc-shaped micellæ (see p. 411). It is true that even in the case of the double refraction of gelatine sols (see p. 545) there was a doubt about its interpretation. Since it can only be produced by powerful mechanical means, a double refraction due to tension and compression is suggested, but the possibility must not be unconditionally excluded that we may be dealing here as well with an orientation of anisotropic particles, only that their departure from sphericity is very small, and only shows itself at great speeds of stirring and large velocity gradients.

With gels, however, this mode of distinction cannot be used. Now very many substances behave as regards double refraction like ordinary glass :—with unilateral pressure an optical behaviour like that of uniaxial negative substances, with unilateral tension as with uniaxial positive substances ; hence Ambronn [3] frequently pursues the idea, that the exceptions to this rule may be referred to the occurrence of double refraction due to orientation of anisotropic particles. He is, of course, well aware that the explanation is not excluded that the double refraction is due in the ordinary way to tension and compression and consequent change in density, only that the physical constants concerned are such as to allow the double refraction to change in sign as compared with glass. An example in which orientation double refraction almost certainly causes departure from the usual tension-compression effect is the behaviour of cherry-gum and some other gels investigated by v. Ebner,[4] and particularly by Ambronn.[5]

[1] Kolloidzeitschr. **6**, 222 (1910).
[2] Verhandl. d. Naturhist. Ver. d. preuss. Rheinlande u. Westfal. **20**, 39 (1863).
[3] Ber. d. kgl. Sächs. Ges. d. Wiss. z. Leipzig, math.-phys. Kl. Naturwissensch. Teil **50**, 1 (1898).
[4] "Untersuchungen über die Ursachen der Anisotropie organischer Substanzen," Leipzig, 1882, p. 66 *et seq.* ; Sitzungsber. d. Wien. Akad. d. Wiss., **97**, II, 39 (1888).
[5] Ber. d. deutsch. bot. Ges. **7**, 103 (1889).

The dry gel of cherry-gum shows under tension and compression a double refraction like that of glass; we may therefore reckon with a normal tension-compression double refraction. But if the gel is allowed to swell in 75 per cent. alcohol or in a moist chamber, and the swollen gel is investigated, quick pressure at first produces a double refraction as with the dry gel, but this gradually passes over into a double refraction of reversed sign. A double refraction of reversed sign is immediately observed if the pressure is applied gradually. If the pressure is released from a gel which has been for some time under pressure, and hence refracts anomalously, the double refraction does not disappear immediately, but instead increases at first and then gradually decreases. Ambronn explains this behaviour as due to the co-existence in swollen cherry-gum of an orientation and tension-compression double refraction, the two having opposite signs. The orientation effect appears gradually, since time is required for the movement of the particles. The double refraction existing in a gel which has been some time under pressure is to be regarded as the sum of the two effects; when the tension-compression effect disappears on removal of the pressure the full value of the orientation effect is observed, which gradually disappears as the particles return to their irregular order.

This superposition of several causes of double refraction appears to exist frequently in the case of other gels, and the result is a complicated behaviour of the directly observed total double refraction. Ambronn[1] investigated several examples in which a rod effect acts together with the effect of anisotropy of the particles themselves, a combination such as is met with in stream double refraction in sols; except that in the latter case the two effects cannot be separated, since the micellæ cannot be simply embedded in another dispersion medium. In the case of gels Ambronn proceeds to soak the dry gels with liquids of various refractive indices and to test the double refraction occurring upon extension and the dispersion for various colours. He is thus able to separate the effect due to the difference in refractive indices from that independent of the latter, and thus to decide to what extent a rod double refraction is present, and what is the nature of the double refraction due to the particles themselves. Rods of *celloidin* and *cellulose* were examined, the latter being prepared from the former by denitration with ammonium sulphide. It appeared that the behaviour of celloidin was due to the superposition of a (necessarily) positive rod effect upon a negative double refraction of the particles themselves. In the case of cellulose, on the other hand, both effects were present and of positive sign. Ambronn concludes that cellulose probably consists of anisotropic particles, the longitudinal axis of which coincides with the axis of the fibre; we shall see (p. 725) to how great an extent Debye and Scherrer's method has confirmed this.

It may perhaps be remarked that in the case of gels we must doubtless always reckon fundamentally with the possibility of a pure tension-compression effect as well. Hence under certain circumstances a gel with spherical isotropic micellæ might behave as if rod and orientation effects were superimposed in it; a displacement in the arrangement of the spheres might produce rod-shaped interspaces, and the change in density of the

[1] Ber. d. kgl. Sächs. Ges. d. Wiss. z. Leipzig, math.-phys. Kl. **63,** 249, 402 (1911); Kolloidzeitschr. **9,** 147 (1911); **18,** 90, 273 (1916); **20,** 173 (1917); Nachr. d. kgl. Ges. d. Wiss. z. Göttingen, math.-phys. Kl. 1919; see also *Hans Ambronn*, Kolloidzeitschr. **13,** 200 (1913).

spheres produced by tension and compression might give them a double refraction of their own.[1]

In Ambronn's experiments on celloidin and cellulose just discussed, the double refraction, being composed, in the manner described, of two effects, depends in a rather complicated way upon the amount of extension to which the strips of gel are subjected. With other gels—gelatine and caoutchouc—simpler relations have in part been found with the mechanical load and the micella content,[2] but it does not appear to be of much use discussing them in detail, until the meaning of this double refraction is better known. Only the following may be remarked. There is no simple connexion between the double refraction and the moduli of elasticity of gels; for the influences of salts and other substances upon the two effects are largely independent of one another.[3] It is therefore intelligible that the mechanical relaxation time cannot be straight-away determined from the time-change in the double refraction (cf. p. 719).[4]

Concerning other optical properties it may be mentioned that gelatines in their natural state rotate the plane of polarized light—an influence that is of course taken into account in the experiments on double refraction above referred to. Double refraction and optical rotation are affected by salts in the same sense; chlorides and nitrates depress both, while sulphates do not affect them.

Leick also determined in the course of his investigations the indices of refraction of various gelatine gels.

Size, Shape, and State of Aggregation of the Micellæ in Gels

It has been already pointed out in discussing the structure of gels (p. 660) that the clear appearance of gels can only be understood if the micellæ are sub- or amicronic. As soon as a coarser degree of dispersity is present, for instance, upon soaking with a liquid, as in Bütschli's experiments, the gel becomes opaque as in the opacity-point of a silicic acid gel. That the ultramicroscopic investigation of gelatine (see p. 661) leads to the same result has already been shown earlier. The micellæ might easily be considerably larger without endangering the structure and solidity, provided that, being separated only by ultramicroscopic films of liquid, they can attract one another. The gels, however, become opaque. As remarked above (p. 658), it may be regarded as questionable as to how far these opaque gels are to be regarded as gels in the strict sense, and how far they are not coagels.

In the ultramicroscopic investigation of silicic acid and gelatine gels nothing was observed which told against a practically spherical form.

[1] A great deal of work has been done upon the optical effects of stress in glass and celluloid by mechanical engineers with a view to elucidating the stresses occurring in bodies of forms not amenable to calculation. A paper by *Coker, Chakko* and *Ahmed* [J. Inst. Mech. Eng., 1921, I, 365] describes experiments with celluloid and refers to earlier work, in particular the fundamental mathematical investigations of *L. N. G. Filon*.—[*Trans.*]

[2] *v. Bjerkén*, Wied. Ann. **43**, 808 (1891); *Leick, loc. cit.* p. 717.

[3] *Leick, loc. cit.* p. 717.

[4] Concerning double refraction caused in a gelatine gel by the passage of an electric current, see *Malcolm*, Phil. Mag. (6), **12**, 548 (1906).

If, as Hermann Ambronn assumes, the double refraction of gelatine sols (see p. 545) should depend upon an orientation of anisotropic particles, they must depart but very little from the spherical form, otherwise no reason could be seen why such large gradients of velocity are necessary to produce double refraction in contrast to the ease with which stream double refraction is usually set up in sols. Micellæ which depart greatly from spherical form are, according to the investigations of Zsigmondy and Bachmann,[1] present in the coagels to which soap solutions set. Upon coagulation the soap sol or gel is permeated by innumerable threads. These often appear suddenly in their full length (cf. p. 614), so that one must assume that they are already present in the sol or gel in amicronic dimensions, and grow to submicronic upon coagulation. Figs. 136 and 137 (Plate IV) show the ultramicroscopic view of a potassium palmitate and a sodium oleate coagel, Fig. 138 A to E (see Plate IV) the changes experienced by a potassium stearate coagel in course of time passing over various stages of coarsening to the formation of unmistakable crystals. With palmitates, stearates, and oleates, thread-like micellæ were observed. In view of their considerable size, the gels are white and opaque, when the network of threads is very dense; if it is thinned a little as by warming, the coagel is transformed again into a transparent gel in which threads are formed (p. 707). These threads one will regard as the finest crystals, if we are not justified in assuming the existence of anisotropic, amorphous solids (see p. 725). Similar gels—or coagels—with thread-like particles were obtained by Flade[2] upon the jelly-like solidification of solutions of *barium malonate* in methyl alcohol (in presence of some glycerine).

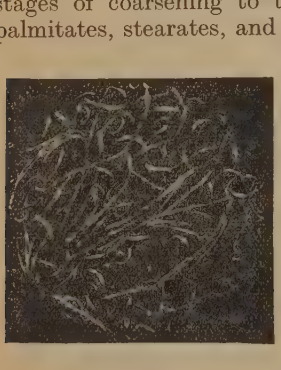


Fig. 136.

If we have here coagels, and on the grounds of their production and transformation also gels, the micellæ of which may be regarded as small crystals, we also have conversely crystals, whose power of taking up water is exactly similar to swelling, so that they cannot be fundamentally distinguished from gels. In this case it is throughout a matter of crystals of substances of high molecular weight, such as the crystalline proteins, polysaccharides, and others; the crystalline vitellin, edestin, oxyhæmoglobin and carboxy-hæmoglobin, amylodextrin and others. Katz[3] has examined their behaviour more closely. The dry crystals take up water, remaining perfectly clear and becoming up to 20 per cent. larger, the crystalline angles changing sensibly. They all swell to a limited extent. The vapour-pressure curve has throughout the form shown in Fig. 128.

Experiments by Debye and Scherrer's method have given decisive information concerning the form of the micellæ, although work has only just begun in this field. It has been shown that, as with the sols, all possibilities exist, and that no conclusions can be drawn concerning the state of aggregation of the gel micellæ from the external appearance.

[1] *loc. cit.* p. 614. These results were confirmed and extended by *Darke, McBain and Salmon*, Proc. Roy. Soc. **98**, A, 395 (1921).

[2] Zeitschr. f. anorg. Chemie, **82**, 173 (1913).

[3] Kolloidchem. Beihefte **9**, 77 *et seq.* (1917).

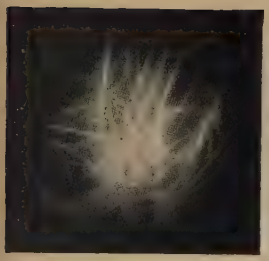


FIG. 137.

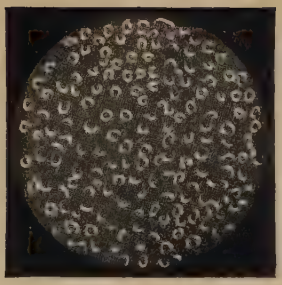


FIG. 138A.

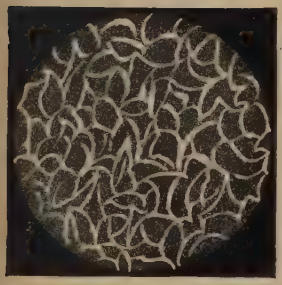


FIG. 138B.

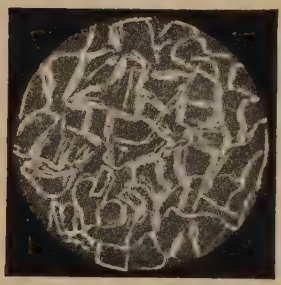


FIG. 138C.

FIG. 138D.

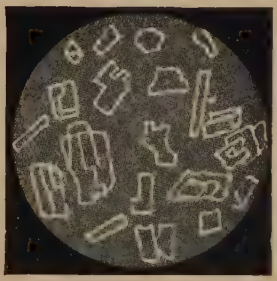


FIG. 138E.

To face page 724.]

Thus Scherrer [1] and R. O. Herzog and W. Jancke [2] found simultaneously that *cellulose* is crystalline, and hence gives a spectrum with well-marked lines. Plate V, Fig. 139, shows that of crumpled ramie fibres. The same lines are observed with celluloses of quite different origin and different degrees of purity, such as paper, wood, ramie, etc. The position of the lines may be calculated upon the assumption of a rhombic space lattice. Silk also has a line spectrum, the lines of which are less sharp (see Fig. 141, Plate V). Wool has not; it proves to be amorphous. Fig. 143 on Plate V is the radio-spectrogram of human hair, which behaves similarly. The various kinds of starch were crystalline, glycogen amorphous. Gelatine shows, according to Scherrer, two flat maxima and a uniform blackening, from which he would like to conclude that gelatine is a mixture of two amorphous substances. Caoutchouc behaves similarly.[3] According to Kyropoulos, a silicic acid gel (cf. Plate I, Fig. 74, p. 334) gives the radio-spectrogram of an amorphous substance, while Scherrer found with aged SiO_2 and SnO_2 gels, in addition to general blackening, interference lines which point to the existence of crystals together with amorphous matter. It may also be recalled that amorphous carbon shows very broad maxima, which, however, lie at the same points as with graphite,[4] so that, as above in the case of V_2O_5 (p. 414), we must assume "amorphous" carbon to be extremely finely crystalline, with an arrangement of the valencies similar to that of graphite. This corresponds to that in a benzene ring, so that amorphous carbon is to be regarded, as it were, as aromatic, with which its strong adsorptive power might be connected (cf. p. 190).

It is noteworthy that not only are cases known, such as that of cellulose, in which a substance is crystalline, although from its general character one would regard it as amorphous, but also the converse: substances which one might take to be crystals from their appearance, but which show no line spectrum. To these belong the "crystalline" proteins, such as fibrin, oxyhæmoglobin, and others. Fig. 142 in Plate V is the radio-spectrogram of a globulin from horse-serum [5]; it had a definitely crystalline appearance.

If this result should be confirmed, there would be various ways of explaining it. In the first place it is probable that substances of high molecular weight consist of mixtures of several nearly related substances.[6] We should thus have isomorphous mixtures, in which perhaps the different sizes of the structural units or differences in degree of swelling produce distortions of the lattice planes and prevent any regular interference taking place.

A second, closely allied possibility consists in our having to distinguish from crystals *anisotropic amorphous solids*. They would be formed in the case, say, of molecules of a very decided, perhaps elongated form, when such molecules unite together in loosely arranged groups, without the atoms falling into the strict arrangement of the space lattice. Such an anisotropic amorphous solid might be compared, although not quite accurately, with a bundle of lead-pencils, in which the various pencils project to greater or smaller distances, and also the imprints of the maker may lie anywhere, while in a crystal the strictest order would reign. Such an anisotropic

[1] *Zsigmondy*, "Kolloidchemie," 3rd Ed., p. 408 *et seq.*
[2] Zeitschr. f. Physik, **3**, 196 (1920); Ber. d. deutsch. chem. Ges. **53**, 2162 (1920).
[3] *Scherrer* in *Zsigmondy's* "Kolloidchemie," 3rd Ed., p. 409.
[4] *Debye* and *Scherrer*, Physik. Zeitschr. **18**, 300 *et seq.* (1917).
[5] *R. O. Herzog* and *W. Jancke*, Die Naturwissenschaften, **9**, 320 (1921).
[6] *Emil Fischer*, Ber. d. deutsch. chem. Ges. **52**, 814 (1919); *R. O. Herzog* and *K. Becker*, Zeitschr. f. physiol. Chemie, **112**, 231 (1920).

amorphous solid would have the external form of a rod or thread, indeed even of a crystal, but nevertheless would give no line radio-spectrum. The assumption of such structures is by no means arbitrary. If, with Bose,[1] we explain anisotropic liquids (so-called "liquid crystals") by assuming that in them groups of elongated, similarly orientated molecules are formed, then we should obtain an anisotropic amorphous solid if a liquid crystal of this kind were converted into a glass by sudden cooling. That liquid crystals behave towards X-rays as if amorphous is known.[2] Groth[3] already earlier required the existence of anisotropic amorphous solids, on the ground of the assumption of non-spherical molecules. In the case of the particles of V_2O_5 sols, in connexion with which Diesselhorst and Freundlich[4] first discussed this view in detail, it has been shown, it is true, that the particles must be regarded as very fine crystals (cf. p. 567). But in the case of fibrin and the other substances mentioned, the view of an anisotropic amorphous solid might be maintained with justification. They are nothing else than the structures described by Rinne[5] as "all-but-crystals" (*Fastkristalle*) and for which he gives a very characteristic description clearly differentiating them from crystals.

As a third possibility that would explain the appearance of crystalline formations with absence of a line radio-spectrum, we may name that in which the structural units of the crystals of substances of high molecular weight are so great, the spatial periodicities so far apart, that no interference can occur with X-rays. One would then have to make use of ultra-violet light.

By means of radio-spectroscopy, not only may size (see p. 333), shape, and state of aggregation of the micellæ of a gel be determined, but also their arrangement in the gel. For this purpose, using Debye and Scherrer's arrangement, we must not examine samples consisting of the irregular powder of the pulverized (or even crumpled-up) gel, but pieces of the gel as regularly arranged as possible; thus in the case of cellulose, for instance, instead of the crumpled ramie threads (Fig. 139, Plate V), a bundle of parallel ramie threads. We then get (see Fig. 140 in Plate V), instead of the usual Debye-Scherrer spectrogram with circular interference lines, a spectrum with regularly arranged points, or more correctly, spots.[6] The rule is a *four-point spectrum*, in which four points arise from the single interference circle. These lie at the corners of a rectangle, the middle point of which is on the path of the X-ray beam. Under various conditions the four-point spectrum may condense to a two-point; here the two points lie equidistant above and below, or right and left, of the point where the X-ray beam meets the film. Polanyi[7] was able to show that a four-point spectrum of this kind must be formed when instead of an orderless crystal powder, in which the crystals may have any positions whatever, we have crystals arranged in a regular manner about an axis. With fibres this axis is the fibre axis. If the axis of the fibres coincides with an axis of the crystal

[1] Physik. Zeitschr. **9**, 708 (1908); **10**, 32, 230 (1909); see also *Nernst*, Zeitschr. f. Elektrochemie, **16**, 702 (1900); *Mauguin*, Compt. rendu, **152**, 1680 (1911).

[2] *Van der Lingen*, Verh. d. deutsch. physik. Ges. **15**, 913 (1913).

[3] Zeitschr. f. Kristallogr. **54**, 498 (1915).

[4] Physik. Zeitschr. **16**, 419 (1915); Internat. Zeitschr. f. phys.-chem. Biologie, **3**, 46 (1916).

[5] Die Naturwissenschaften, **5**, 49 (1917).

[6] *Scherrer* in *Zsigmondy*, "Kolloidchemie," 3rd Ed., pp. 408–409; *R. O. Herzog, W. Jancke*, and *Polanyi*, Zeitschr. f. Physik, **3**, 343 (1920).

[7] Die Naturwissenschaften, **9**, 337 (1921); Zeitschr. f. Physik, **7**, 149 (1921).

FIG. 139.—Ramie Threads (Crumpled).

FIG. 140.—Ramie Threads (Parallel).

FIG. 141.—Silk (Parallel).

FIG. 142.—Serum Globulin.

FIG. 143.—Human Hair.

To face page 726.]

system of the crystals, then we get spectra the points of which are arranged regularly on a straight line to right and left of the centre. This case appears to be fairly frequent.[1]

It would appear as if an amorphous gel, such as that of gelatine, is not strictly isotropic in fairly large units of space, but that in it a certain arrangement, or certain directed strains, exist.

In such a gel gas bubbles may be generated by mixing the sol before solidification with some carbonate solution, and then allowing dilute acid to diffuse into the gel when set. These gas bubbles are not spherical, as one might suppose if the gel were isotropic down to the smallest spatial units, but almost invariably lens-shaped; this means, that the resistance found by the gas in developing is greater at right-angles to the lens surface than in it. That the form of the gas bubbles is influenced in this sense appears from the fact that when a pressure is exerted upon a gel cylinder in both directions along the axis, the planes of the lenses are all set at right-angles to the axis. Hence in the gel there exist over finite distances differences in the resistance which gas bubbles experience upon being generated. Over a sensible distance a definite direction of cleavage is preferred. Hatschek [2] has attempted to determine the position of the lens-plane for a large number of gas bubbles in a gel that had set with as little disturbance as possible, and to decide whether throughout the whole gel certain directions of cleavage were preferred, or whether they are distributed irregularly according to probability. These first experiments did not lead to any definite results.[3]

That strains exist in gels also appears from the fact that when a completely dried silicic acid gel is dipped into water, it bursts into small pieces.[4]

Diffusion in Gels

The solid-liquid character, which already appeared so prominently in the elastic properties, again becomes noticeable in a very important and surprising manner in diffusion in gels and hence in the reactions taking place in gels. Originally it seemed as if gels did not differ in any way from liquids as regards the diffusion of dissolved substances. Thus Th. Graham [5] stated that common salt diffused in a gelatine gel just as quickly as in pure water; de Vries [6] found the same for copper sulphate in a gelatine gel and for potassium chromate in a silicic acid gel, Voigtländer [7] for a series of different acids in agar gels.

Upon further investigation [8] of these phenomena it appeared that this

[1] Very rapid development is going on in this field. See *Bragg*, Proc. Phys. Soc. **34**, 33 (1921), and the report by *Tutton* in Chem. Soc. Annual Reports, 1921, p. 210. —[*Trans.*]

[2] Kolloidzeitschr. **15**, 226 (1914).

[3] See also *Bütschli's* investigations of the structures around and between air-bubbles in gels. ["Untersuchungen über Strukturen," Leipzig, 1898, p. 158 *et seq.*, further Verh. d. Naturhist.-mediz. Ver. Heidelberg, N.F. **7**, 653 (1904)].

[4] *Bütschli*, "Untersuchungen über Strukturen," Leipzig, 1898, p. 83; *Zsigmondy*, "Kolloidchemie," 3rd Ed., p. 236.

[5] Lieb. Ann. **121**, 5 and 29 (1862).

[6] Rec. Trav. Chim. d. Pays-Bas, **3**, 375 (1884).

[7] Zeitschr. f. physik. Chemie, **3**, 316 (1889).

[8] *Nell*, Ann. d. Physik (4), **18**, 323 (1905); *Bechhold* and *Ziegler*, Zeitschr. f. physik. Chemie, **56**, 105 (1906); *O. v. Fürth* and *Bubanović*, Biochem. Zeitschr. **90**, 265 (1918); **92**, 139 (1918); then also *Durrant*, Proc. Roy. Soc. **78**, A, 342 (1906); *Vanzetti*, Zeitschr. f. Elektrochemie, **20**, 570 (1914).

behaviour is only true in certain limiting cases; in not too concentrated gels it holds approximately for a series of neutral salts, such as the chlorides of the alkali metals, alkaline earths, and many heavy metals. Here the different degrees of hydration appear to produce little effect. On the other hand, strong divergences already appear with sulphates, which in gelatine and agar gels diffuse far more slowly than in pure water, and then, in particular, almost generally for the acids, and in part also for the bases; only ammonia diffuses in gels as fast as in pure water. In concentrated agar and gelatine gels (over 10 per cent.) the velocity of diffusion of NaCl also falls, a substance that in dilute gels shows only a very small change.[1] All substances of high molecular weight diffuse more slowly in gels. Thus the experiments of R. O. Herzog and Polotzky [2] teach us, that the diffusion constants of all dyes examined were already considerably lower in 5 per cent. gelatine gels (cf. Table 144, p. 548). This is the more pronounced, the higher the molecular weight of the dissolved substance, until finally for colloidally dissolved substances the gels serve as filters, which only allow the dispersion medium to pass. This was described earlier in connection with the ultra-filters (cf. p. 379) and the behaviour of silicic acid gels (cf. p. 687). It was already pointed out there that by increasing the disperse phase content of the gel the permeability for colloidally dissolved substances of various sizes of particle can be graded systematically. The power of diffusing in a concentrated gel (about 20 per cent. gelatine) may serve as a means of deciding whether a dissolved substance is truly or colloidally dissolved, and Ruhland [3] has successfully characterized in this way the aqueous solutions of a very large number of dyes.

If for the present we leave aside the substances which affect swelling in a pronounced fashion, or otherwise enter into chemical interaction with the gel micellæ, we gain the impression that the mechanical properties of the gel are important for diffusion. Moreover, everything tells in favour of the intermicellar liquid films being essentially concerned. If these are thick enough, as in the case of dilute gels, and if the molecular weight of the dissolved substance is small enough, diffusion is little different from that in the free dispersion medium. The narrower the capillaries (in concentrated gels), and the greater the molecular weight of the dissolved substance, the stronger is the purely mechanical modification of diffusion and the clearer the appearance of other influences. Then we have above all to reckon with the possible adsorption of the dissolved substance by the gel micellæ. If adsorption is negative, this may lead to a surprising consequence. Assuming that in the concentrated gel the water is present practically only as adsorption envelope, the dissolved substance might be largely prevented from passing through, although it is soluble in water and diffuses rapidly enough [4] (cf. p. 745). Perhaps the slow diffusion of sulphates depends in part upon this, since some data exist which tell in favour of their negative adsorption (p. 691).

The particular behaviour of the acids is probably caused by the same circumstances which distinguish them in respect of swelling (cf. p. 690).

The substances which enter into reaction with the gel micellæ in any preferential fashion and hence show a divergent behaviour on diffusion, are also those which, as may readily be understood, are able to change the

[1] *Bechhold* and *Ziegler, loc. cit.* p. 727.
[2] *loc. cit.* p. 546.
[3] Jahrbücher f. wiss. Botanik, **51**, 376 (1912).
[4] *A. Nathansohn,* "Stoffwechsel der Pflanzen," Leipzig, 1910, pp. 102–3.

properties of gels as diffusion paths for other substances. According to experiments by Bechhold and Ziegler,[1] sodium sulphate, glucose, glycerine, and alcohol, appear to diminish the permeability of gelatine and agar jellies for dyes and electrolytes, while urea increases it. An inhibition of the diffusion of acids in gelatine gels by sugar is unmistakably present according to E. A. Graham and Miss H. T. Graham.[2] A connexion with the influence of these substances upon the sol-gel transformation must be assumed, although the parallelism is not strict.

As may be expected after what has been said, the investigation of the conductivity of electrolytes in gels leads to no results of importance. The differences that are found as compared with the behaviour in aqueous solution may be referred to the fact that in accordance with the lower diffusion coefficients the mobility of the ions is diminished[3] or that the degree of dissociation is different or that the concentration has changed in consequence of positive or negative adsorption.[4] That this is then also true for concentrated sols, and that sols and gels have equal conductivity, has already been described earlier (p. 708).

Chemical Reactions in Gels

Since truly dissolved substances diffuse in gels with a velocity which only differs but little from that occurring in a pure solution, all reactions between such substances can be made to take place in a gel. In this respect the gel fully corresponds to a liquid. In another respect, on the other hand, it completely resembles a solid substance; the motion of the dissolved substance takes place by diffusion alone, convection is almost entirely absent, since the molecules of the solvent as elementary parts of the adsorption envelope and in the amicronic capillaries have to a great extent lost their free mobility. We have therefore conditions such as exist when the chemical reactions take place in an amorphous solid, for example, a glass. Chemical reactions free from every influence of convection take place under conditions which, especially in the case of processes which lead to the separation of a solid phase, are never or only very seldom met with in a free liquid.

Let us consider the sequence of processes (p. 459) which are to be assumed as taking place when a solid substance separates from a liquid, and ask which of them will be more strongly influenced by its taking place in a gel, where therefore convection is absent and the gel micellæ exert an influence. It is here assumed that the micellæ of the gels react sluggishly, as in the case of a silicic acid gel, that they have therefore no tendency to lively chemical reaction; further, that the chemical reaction leading to the formation of the solid substance takes place rapidly, so that the time required for the formation of the molecule of the solid reaction product may be neglected. Nuclei of the solid phase will be formed in the gel just as in the free liquid. It is true that we must take into account the fact that, according to Tammann's experiments (p. 321), sluggishly reactive, solid powders may greatly alter the velocity of formation of nuclei, in

[1] *loc. cit.* p. 727.

[2] Journ. Amer. Chem. Soc. **40**, 1900 (1918).

[3] Whereby however it must be remembered that the *Nernst* relation between these two quantities is not fulfilled, especially in the case of strongly hydrated ions (see *O. v. Fürth* and *Bubanović, loc. cit.* p. 727).

[4] See *Dumanski, loc. cit.* p. 691.

particular increase it; it is therefore possible that the number of nuclei may be considerably increased by the presence of the micellæ. From the nuclei arise larger amorphous flakes, or, if we are originally only dealing with crystal nuclei, larger crystals; we will suppose the latter for the present. They grow on account of the diffusion towards the nuclei of the molecules of the substance produced by the reaction. In the gel, therefore, a ring is formed around each nucleus; for since in the immediate neighbourhood of the nucleus all molecules of the reaction product have soon joined the nucleus, new molecules also diffuse towards the latter from some distance around, and hence, in the more distant surroundings of the nucleus, the solution is depleted of molecules. On account of its size the nucleus will execute a Brownian motion of only a small range and hence will keep its position practically unaltered. The small crystal finds itself under the most favourable conditions imaginable for quiet growth, which can be obtained artificially only with difficulty by suspending a crystal in a solution but slightly supersaturated. It rests quietly encircled by a supersaturated solution, the supersaturation of which can only slowly be removed by diffusion. This, however, does not mean that the growth of the crystal in the gel will be uniform on all sides. For according to what was said above (p. 727) concerning the shape of gas bubbles in gels, it is quite possible, indeed probable, that the amount diffusing inwards in a certain plane will exceed that diffusing from other directions. The crystal nucleus may further be adsorbed on the gel micella and hence in this way as well asymmetry may be brought into the conditions of diffusion. How much more unfavourable are the conditions for steady growth in a free liquid hardly needs to be discussed; the larger crystals settle under the influence of gravity, and become removed from the uniform conditions for growth existing in the interior of the liquid. If this is strongly stirred, two or more nuclei may unite to coarser, irregularly formed crystals; as soon as a certain size is exceeded, the association of particles is favoured by stirring (see p. 437).

According to these considerations it is therefore to be expected that under some conditions particularly beautiful and well-formed crystals will be produced in gels. This is actually the case, as was especially proved by Hatschek.[1] He prepared, for example, gold crystals in a silicic acid gel. The gel prepared in the usual way originally contained some dissolved gold chloride; after the gel had set he allowed a reducing agent to diffuse into it from outside. If he used reducing agents in solution, such as sodium sulphite, formic acid + ammonia, or oxalic acid, the solutions had to be more concentrated than the solutions contained in the gel in order that the gold should be deposited in the gel, otherwise the $AuCl_3$ diffused outwards and was reduced outside the gel. He also used gaseous reducing agents, such as carbon monoxide, illuminating gas, acetylene, by suspending the gel containing $AuCl_3$ in a globe containing the gas in question. According to the nature of the reducing agent, the concentration and temperature conditions, the form of the separated gold was different, since the conditions of formation of nuclei and of crystallization were different. By reduction with oxalic acid the gold already separated at room temperature

[1] Kolloidzeitschr. **10,** 77 (1912); *Hatschek* and *A. L. Simon, ibid.* **10,** 265 (1912) (Experiments on gold crystals). Regarding surface-like silver crystals upon penetration of $AgNO_3$ into a gelatine gel containing $FeSO_4$, see *Liesegang*, Kolloidzeitschr. **17,** 141 (1915); further *H. N. Holmes*, Journ. Franklin Inst. **184,** 743 (1917), cited from Kolloidzeitschr. **25,** 213 (1919).

in the form of well-shaped small crystals. With the same reducing agent at about 50° to 70° highly polished gold plates were formed with diameters up to 2 mm.; these experiments succeeded with certainty with the non-dialysed gels prepared from waterglass solution and still containing NaCl, which are more rigid and stiffer than the dialysed. It is unnecessary to remark that one cannot succeed in preparing such large crystals in the free liquid by the reduction of the gold salts.

If the concentration of the solution in the gel is greater than in the external solution, the $AuCl_3$ diffuses into the external solution, and the gold separates—with oxalic acid, for example—as a continuous leaf upon the surface of the gel.

Hatschek pointed out how completely the various forms that can be observed in a silicic acid gel resemble the natural appearance of the gold in gold-bearing quartz: large leaf-shaped crystals, often on the surface, layers of finely divided gold—with which we shall deal immediately—separation of gold and carbon side by side (as observed in silicic acid gels upon reduction with hydrocarbons), and so on. According to this it is very probable that gold-bearing quartz has been formed from silicic acid gels containing gold salts in solution. In the case of a large number of difficultly soluble substances, such as lead chloride, calcium sulphate, copper and calcium phosphates, Hatschek [1] obtained large crystals or crystal aggregates in silicic acid gels when he allowed suitable solutions to interact in the gel (for instance, NaCl in the gel, $Pb(NO_3)_2$ outside; Na_2SO_4 in the gel, $CaCl_2$ outside). A. L. Simon [2] also obtained lead trees in beautiful large crystalline form by reducing a $Pb(NO_3)_2$ solution in the gel on a zinc rod. In any case separation in a silicic acid gel is a noteworthy method of obtaining large crystals of a difficultly soluble substance.

This formation of large crystals assumes: not too large a velocity of formation of nuclei, a sufficiently large velocity of crystallization, and hence a gel the micellæ of which do not exert a strong protective action, as is known to be the case with silicic acid (cf. p. 598). Accordingly Hatschek found also in the comparatively little protective agar gel the tendency to the formation of large crystals, but not in the strongly protective gelatine gel. In this, as in the case of most other gels, particularly of organic substances, a decided protective action is present; the crystallization velocity is small (cf. p. 596). There is, however, no reason why the velocity of formation of nuclei should not be large; hence with the small crystallization velocity a considerable amount of the separating solid will appear as nuclei which do not grow into larger crystals. The rigidity of the gel has the further consequence that the nuclei remain where they have been formed. Since the conditions of the velocity of formation of nuclei in gels will be in general fairly regular, the nuclei are very evenly distributed. Hence the new solid phase permeates the gel uniformly, whether in colloidal solution or in coarse distribution. Thus Hatschek and A. L. Simon describe cases of the reduction of gold (e.g. in reduction by formic acid + ammonia), in which the gold, distributed colloidally, colours the gel uniformly violet, while under other conditions distinct layers of coarser gold micellæ are formed. Further examples of the uniform deposition of nuclei will be discussed later (p. 741).

Occasionally the phenomenon appears, on the separation of a solid phase in the gel, that the deposition is not uniformly distributed in the whole

[1] *loc. cit.* p. 730. [2] Kolloidzeitschr. **12**, 171 (1913).

gel, but comes out in regular layers. These layers, first described by Liesegang, are in many respects so important that they will be treated separately (see below).

The diverse manner in which the predominance of diffusion in a gel may influence the processes taking place in it may be shown by an example of another sort. If a dilute solution of lactic acid be allowed to act upon a finely ground, intimate mixture of calcium carbonate and calcium phosphate, the ratio between $CaCO_3$ and $Ca_3(PO_4)_2$ is displaced to the disadvantage of the solid $CaCO_3$, since the CO_2 set free escapes and the equilibrium as regards the carbonate is continually displaced, while this is not the case with the phosphate.

But if the mixture of the two calcium salts is uniformly stirred up in a gelatine sol, and after the latter has solidified the acid solution is allowed to diffuse in from one side, one finds, when the ratio of $CaCO_3$ to $Ca_3(PO_4)_2$ for the undissolved part of the calcium salts is now determined from time to time, that this ratio has remained unaltered. This is explained by the acid not being able to diffuse further until it has dissolved up every particle of $CaCO_3$ and $Ca_3(PO_4)_2$ which it finds on its way. Each grain forms a diffusion ring, into which the acid penetrates; it cannot penetrate the whole gel undisturbed and displace the ratio between the two salts, as is possible in the case of a mechanical mixture of the two.

Liesegang[1] performed these experiments in order to show that an acidosis, an increased tendency to the formation of acid in the organism, actually causes puerperal osteomalacy, a disease in which the lime content of the bones is diminished. One felt compelled to doubt this when the first described experiment was performed in which the lactic acid was allowed to act upon finely ground and purified ox bones, and a displacement in the ratio of the two calcium salts was observed, which does not occur in the disease mentioned. But, as Liesegang showed, the bones, if not finely ground, and provided the acid does not act too long, behave like the gel containing calcium carbonate and phosphate; under the action of the lactic acid the ratio remains unaltered. The connective tissue here plays the part of the jelly in the gelatine experiment.

Liesegang's Rings

As already remarked, it is often observed that a solid phase of a difficultly soluble substance does not separate out uniformly in a gel, but forms regular layers. In the following we will first consider the case in which one reacting substance is dissolved in the gel, while a concentrated solution of the other is applied externally. At the point of contact a copious precipitate of the difficultly soluble substance is at once formed. But the second substance then diffuses further into the gel, and produces in it not a uniform precipitation, but a deposition in regular layers. These layers succeed one another in the direction of diffusion, with their planes at right-angles thereto. In the neighbourhood of the place of entry of the diffusing substance they succeed one another at close intervals, which become progressively wider as the distance increases. This phenomenon was first described by Liesegang,[2] who recognized its importance for many

[1] Zentralbl. f. Gynäkologie, **39**, Nr. 15 (1915).

[2] Naturwiss. Wochenschr. **11**, 353 (1896); "Chemische Reaktionen in Gallerten," Düsseldorf, 1898; "Ueber die Schichtungen bei Diffusionen," Leipzig, 1907. Zeitschr. f. anorg. Chemie, **48**, 364 (1906); Zeitschr. f. physik. Chemie, **59**, 444 (1907); **75**,

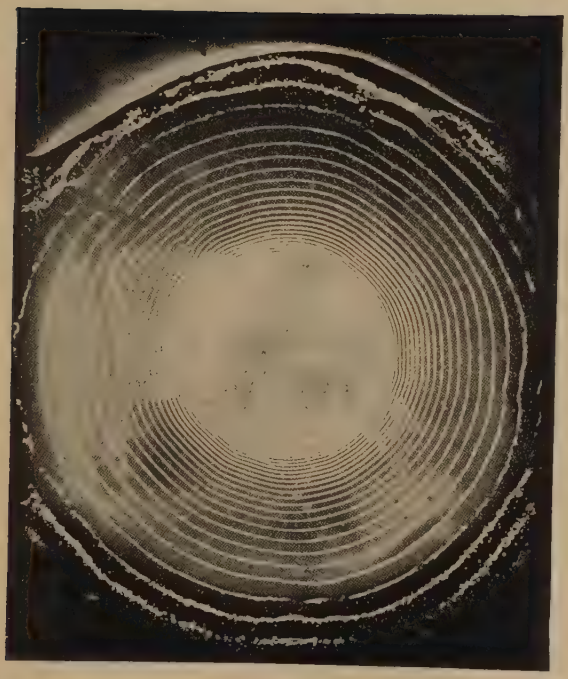


FIG. 144.

To face page 732.]

natural processes, and himself followed up in detail its occurrence especially in the fields of geology and mineralogy. In Fig. 144 (see Plate VI) such Liesegang "rings" (*Schichtungen*) are reproduced, the example being chosen in which Liesegang first observed them, and which is easily realized. The gelatine gel (2 to 3 per cent.) contains potassium bichromate (or ammonium bichromate : 0·1 per cent.). It is spread out on a glass plate or placed in a test-tube. Then a drop of a very concentrated (50 per cent.) $AgNO_3$ solution is brought on to the glass plate coated with the gel or poured in a layer over the gel in the test-tube. The gelatine must not be too pure, but must contain some acid or gelatose. Liesegang [1] recommends, for example, a mixture of 50 c.c. of a 10 per cent. gelatine solution, 20 c.c. of a 10 per cent. gelatose solution, and 30 c.c. of water as a suitable gel ; some acid must also be present. An old gelatine is hence sometimes more suitable than a fresh sample.

An explanation of this phenomenon, in any way complete, has not yet been found. When processes, the time-course of which is aperiodic, succeed one another, they may produce rhythmical effects if the second process only begins when a threshold value is passed. We may think, for instance, of a uniform flow of water into a cistern which is so arranged that the water only flows away through a waste pipe when a certain level is reached. With the Liesegang rings, the diffusion of the substance entering the gelatine proceeds aperiodically, likewise the formation of the reaction products. But this does not separate in proportion to the velocity with which it is formed. On the contrary, if we consider the series of phenomena which we must assume to take place upon the separation of a solid phase (see p. 459), we meet with two processes in which a distinct threshold value is present. Firstly, the velocity of formation of nuclei ; the velocity with which the nuclei of a solid phase are formed increases indeed extremely rapidly with the supersaturation, so that below a certain supersaturation it is frequently equal to zero (see p. 321). Secondly, the coagulation velocity or rate of coarsening, the rate at which the amicronic particles associate to submicronic or micronic. This velocity has in the first place frequently an autocatalytic course, but also a very large concentration coefficient of the coagulating electrolyte concentration (see p. 441). The coagulation may therefore practically not occur below a certain electrolyte concentration, and occur very strongly at a slightly higher one. Indeed, the rate of coarsening, as we shall discuss immediately, may also cause in a more indirect manner a stronger growth and the formation of a layer only from a certain concentration and size of nucleus onwards.

Obviously, both processes—velocity of formation of nuclei and coagulation velocity—could cause the rhythmic precipitation, since they have distinct threshold values. Whether both must be taken into account, whether one of them only by preference, is still difficult to decide. The theory of the phenomenon proposed by Wilhelm Ostwald [2] assumes the threshold value of the rate of formation of nuclei as sole cause, or, from

371 (1910) ; **88,** 1 (1914) ; Kolloidzeitschr. **2,** 70 (1907) ; **12,** 74, 269 (1913) ; **14,** 31 (1914) ; **16,** 20, 76 (1915) ; Arch. f. Entwickelungsmechanik, **33,** 328 (1911). Further also *Morse* and *Pierce*, Zeitschr. f. physik. Chemie, **45,** 589 (1903) ; *Hausmann*, Zeitschr. f. anorg. Chemie, **40,** 110 (1904) ; *F. Köhler*, Kolloidzeitschr. **19,** 65 (1916) ; *H. N. Holmes*, Journ. Amer. Chem. Soc. **40,** 1187 (1918) ; *A. M. Williams* and *McKenzie*, Journ. Chem. Soc. **117,** 844 (1920).

[1] Zeitschr. f. physik. Chemie, **88,** 3 (1914).

[2] Zeitschr. f. physik. Chemie, **23,** 365 (1897) ; "Lehrbuch d. allgem. Chemie," 2nd Ed., II, 2, p. 778 (1899).

Ostwald's point of view, the metastable limit of the separation of crystals (cf. p. 321). We should form a picture of the phenomenon somewhat as follows. The Ag_2CrO_4 (and $Ag_2Cr_2O_7$)[1] formed by the diffusion of the $AgNO_3$ into the gelatine containing bichromate first remains in supersaturated solution, until the rate of formation of nuclei, which increases greatly with the concentration of the supersaturated dissolved substance, has passed a certain threshold value. Then, behind the front of the diffusion current the nuclei of Ag_2CrO_4 separate out, and now not only does supersaturated dissolved Ag_2CrO_4 diffuse from points in front of and behind the region of precipitation, but this region also becomes poorer in $K_2Cr_2O_7$, which diffuses to meet the $AgNO_3$ and, forming with it Ag_2CrO_4, increases the size of the nuclei. In all these processes it must be remembered that the places of chemical reaction are the starting-points of fresh diffusion currents of the substances formed, not only of the easily soluble KNO_3 (or NH_4NO_3) formed in the reaction, but also of the Ag_2CrO_4 which is always in supersaturated solution. Upon diffusing further the $AgNO_3$ penetrates first into a layer which is greatly impoverished as regards $K_2Cr_2O_7$. Hence it is only at a more or less considerable distance from the first deposited layer that the supersaturation and hence the rate of formation of nuclei become so great that a layer of nuclei again separates. The more the $AgNO_3$ is diluted by further diffusion, the greater the distance between the layers.

Many facts are known which cannot be immediately reconciled with this theory.[2] It is true that it is still difficult to decide whether they really contradict it or not, since so little is actually known concerning the velocity of formation of nuclei; this is, indeed, excessively sensitive to small amounts of dissolved and solid foreign substances, and hence it is not easy to decide how far modification of the rate of formation of nuclei may not be able to explain also the facts in question. Thus, it is at first surprising that the nature of the gel plays so important a part in the formation of the layers. Hatschek pointed out cases of this kind; among others, that, with potassium iodide and lead nitrate, good stratifications were obtained in agar gels, but not in silicic acid gels, in which uniformly distributed macroscopic crystals are formed. But it would naturally be possible that we have here an increase in the velocity of formation of nuclei by the gel micellæ, and that it is much less in silicic acid than in agar gels, less than required for the formation of stratifications.

Another objection to the Ostwald theory is more serious.[3] It is often observed that upon repeating the experiment in the same gel a second series of stratifications is formed, superimposed upon the first, and completely independent of it. One would at first expect that the existing particles of the first series would serve as nuclei for the supersaturated solution upon repetition of the experiment, and thus that the layers already present would simply be strengthened. This, by the way, is often actually the case. In other cases, a second series of layers is formed. This may arise from the fact that they are formed in capillary spaces, which are

[1] We must reckon with both, since $Ag_2Cr_2O_7$ can be formed as long as the bichromate is in excess.

[2] Particularly *Bechhold*, Zeitschr. f. physik. Chemie, **52**, 185 (1905); *Liesegang*, *ibid.* **59**, 444 (1907); **75**, 371 (1910); Kolloidzeitschr. **12**, 74 (1913); "Geologische Diffusionen," Dresden, 1913, p. 89; *Hatschek*, Kolloidzeitschr. **9**, 97 (1911); **10**, 124 (1912); **14**, 115 (1914); *F. Köhler*, *loc. cit.* p. 733.

[3] *Liesegang*, *loc. cit.* under [2]; *Hatschek*, *loc. cit.* under [2].

spatially separated from those filled with the first layer; this possibility exists when the rings are produced on plates, but not in test-tubes, in which Hatschek likewise obtained independent formation of layers.

Another possibility is, that the particles of the first series of layers are materially different from the nuclei of the second, that in the latter case perhaps a labile form separates out, which then changes into the form of the first particles. We have in fact to reckon with the possibility that different substances may separate out. According to F. Köhler,[1] besides silver chromate and silver bichromate, ammonium nitrate may also separate, and the NH_4NO_3 can form with the silver chromates anomalous mixed crystals; these are dark to black brown and form the skeleton of the rings. Such transformations, coupled with the separation of solid substances, may also explain the independent formation of layers in another manner. With difficultly soluble substances, namely, very small amounts [2] often suffice to produce Liesegang's rings. Thus small impurities of carbonates and phosphates, such as easily occur in gelatine, for instance, or (in the case of carbonates) are present in water, may give with salts of the heavy metals —say $AgNO_3$, which in this case has been introduced first into the gel— fine layers of Ag_2CO_3 and Ag_3PO_4. If a bichromate solution is subsequently allowed to diffuse in, not only are the Ag_2CrO_4 layers formed, as produced under pure conditions, but the carbonate (or phosphate) layers, which are quite independent of the Ag_2CrO_4 layers, react with the bichromate according to the solubility relations and are transformed into independent Ag_2CrO_4 layers. These layers caused by the impurities may be so fine upon the first penetration of the bichromate solution, that they escape observation, while upon the second entry of bichromate they are sufficiently increased to be seen. But Hatschek mentions an experiment with lead chromate in agar, with the independent formation of layers, in which he regards such sources of disturbance as completely excluded.

Liesegang [3] believes, and it is quite conceivable, that we need not take refuge in special hypotheses, and that the action of the nuclei at first only makes itself felt in the immediate neighbourhood of the nuclei in the first layer. At a further distance the supersaturation may therefore be large enough and continue long enough for new independent nuclei of the second layer to be formed with the velocity of formation of nuclei in the particular case. This, of course, does not exclude, as Hatschek [4] would appear to suppose, that with a sufficiently small velocity of formation of nuclei the diffusion areas formed by the first particles have a very considerable diameter, especially when, as in the example given by Hatschek of the large gold crystals in SiO_2 gels, we have every reason to assume that the velocity of formation of nuclei is not great (cf. p. 730).

The objections just raised disappear to a large extent when we assume that the threshold value caused by the velocity of formation of nuclei is not the sole cause of the phenomenon, but that caused by the coagulation velocity.[5] We should then have the following limiting case. The threshold value of the velocity of formation of nuclei lies so low, that the nuclei of

[1] *loc. cit.* p. 733; see also *F. Köhler*, Zeitschr. f. anorg. Chemie, **96**, 207 (1916).
[2] *Morse* and *Pierce*, *loc. cit.* p. 733.
[3] *loc. cit.* p. 734.
[4] Kolloidzeitschr. **14**, 115 (1914).
[5] *Bechhold*, *loc. cit.* p. 734; further *Freundlich* and *Schucht*, Zeitschr. f. physik. Chemie, **85**, 677 *et seq.* (1913); *Sekera*, Kolloidzeitschr. **27**, 28 (1920).

the solid phase are formed with practically uniform velocity from the reaction product. They at first remain uniformly distributed in the gel in finely dispersed form. Like the micellæ of a sol, they may be coagulated by electrolytes. Above all, the velocity of coagulation rises strongly with the electrolyte concentration, so that in this respect a threshold value exists. The electrolyte solution diffusing in will therefore only produce coagulation when a certain concentration is reached. Then nuclei lying in front of this coagulation layer will also be drawn in, and the electrolyte, diffusing further, again reaches a sufficient concentration and meets with sufficient nuclei some considerable distance on.

The importance of the gel micellæ is here at once evident, since as protective colloids they influence coagulation. That a uniform distribution of small particles instead of layers is more frequently observed in gelatine gels than in those of silicic acid and agar might be connected with the more powerful protective action of the gelatine opposing coagulation. Independent series of layers may be formed, since one coagulation is entirely independent of another, provided that the formation of nuclei alongside other nuclei is possible at all; but this we may be allowed to assume. Very much in favour of a preponderance of coagulation is the following circumstance pointed out by Hatschek.[1] In many layer experiments, such as with lead iodide and calcium carbonate in agar, barium carbonate in gelatine, and others, no empty spaces are observed between the layers, but always a certain amount of the separated reaction product; we get the impression that it is a matter chiefly of a periodic alteration in the degree of dispersity, and less one of the amount of substance separated per unit volume. This obviously compels us to lay particular stress on the coagulation and coarsening of the particles.

It might be objected to this view that the particles are much too firmly embedded in the gel to allow of an association such as is required for coagulation. But actual observation tells in favour of such a possibility. Liesegang, Hatschek, and others, describe the microscopic appearance of the formation of a layer in words from which the conclusion may be drawn that finer particles unite to form coarser ones. And F. Köhler [2] describes how it is possible to see microscopically that newly formed particles pass over considerable distances on account of their Brownian movement. It is perhaps further to be noted that in these experiments considerable concentrations of electrolyte act upon the gels. We must therefore reckon with considerable swelling and shrinkage, and hence with movements of water, which would likewise permit of a certain displacement of nuclei such as is required for coagulation.

All these facts may be interpreted on the grounds of an influence to which Zocher drew my attention. It would be possible that the very small crystal nuclei first formed at first move sensibly, and that they can do so particularly in the direction of the diffusion current, since the gradient of their concentration lies especially in this direction. As long as they are still in motion, they coarsen comparatively slowly, since they always pass over into a less supersaturated solution. This ceases, however, as soon as they have become sufficiently large to be held back in the gel pores. Then the stronger supersaturated solution reaches them, they grow faster, and a ring is formed. With this agrees the fact already observed by F. Köhler,[3] and confirmed by Zocher, which cannot be very easily explained

[1] Kolloidzeitschr. **14** 120 *et seq.* (1914). [2] Kolloidzeitschr. **19**, 85 (1916).
[3] Kolloidzeitschr. **19**, 72 (1916).

in any other way, that the rings—it is here again a matter of silver chromate—under conditions as like in other respects as possible are formed closer together the more concentrated the gelatine gel. The more concentrated the gel, the finer its pores, the smaller the crystals which adhere, the less the spacing of the rings.

The suggestion readily occurs of testing the theories depending upon coagulation or coarsening by looking for the influence of multivalent and strongly adsorbable ions upon the coagulation. But it is difficult to obtain definite results, since the circumstances that may be influenced are so numerous; the gel may be altered, also the velocity of formation of nuclei, the solubility of the difficultly soluble substances, and so on. We will only go into a few effects of foreign substances here. Bechhold [1] noticed that Ag_2CrO_4 separates at once in $AgNO_3$ solution, but experiences an increase in solubility in $K_2Cr_2O_7$ and particularly in $(NH_4)_2Cr_2O_7$ solutions (as also in solutions of other ammonium salts). Since in the double decomposition in the gel NH_4NO_3 is produced from $(NH_4)_2Cr_2O_7$ and $AgNO_3$ and diffuses into the gel, he explains the appearance or at least the favouring of the precipitate-free zones by the effect of the NH_4 salts in raising the solubility. F. Köhler confirms this rise of solubility, and interprets various facts by aid of it; in the first place, that the distance apart of the rings is independent of the chromate concentration, and further, that the ring-formation is sensibly different according as an $AgNO_3$ solution is allowed to diffuse into a gelatine containing chromate, or conversely a chromate solution into $AgNO_3$ in gelatine.

Acids—citric acid has especially been used—cause the appearance of the Ag_2CrO_4 in a strongly disperse red form, while in their absence more granular, dark, coarser crystals separate.[2] Here the increase in solubility of the $Ag_2Cr_2O_7$ by acids likewise plays a part, not less than the change in the properties of the gel.

Until further data decide more strongly in favour of one or other theory of the Liesegang rings, I regard it as probable that all the various possible experimental circumstances do really play a part, and that above all rate of formation of nuclei, coagulation velocity and rate of coarsening must be taken into account.

The layers appear by preference in gels since in their case diffusion undisturbed by convection is most easily obtained. Since this prerequisite is also given in the case of a viscous liquid or of capillaries, one should be able to observe the formation of layers in the latter; this has been confirmed by experiments by Liesegang,[3] Dreaper,[4] H. N. Holmes,[5] and others. Liesegang obtained a flocculation of litmus in layers when the latter was in a viscous but still liquid solution of water-glass, into which concentrated NaOH diffused. And Dreaper found, as also earlier Morse and Pierce,[6] a separation in layers of various solid substances ($PbCl_2$, CuS, and others) in fine capillaries and in tubes filled with sand or kieselguhr.[7]

[1] *loc. cit.* p. 734; concerning further influences of foreign substances see especially *Liesegang*, "Ueber die Schichtungen bei Diffusionen," Düsseldorf, 1907, p. 47 *et seq.*

[2] *Liesegang*, Arch. f. Entwickelungsmechanik, **39**, 362 (1914).

[3] Kolloidzeitschr. **12**, 76 (1913).

[4] Kolloidzeitschr. **14**, 163 (1914).

[5] *loc. cit.* p. 733.

[6] Zeitschr. f. physik. Chemie, **45**, 607 (1903).

[7] Regarding *Liesegang* layers in glasses see, for example, *Endell*, Neues Jahrb. f. Mineral. Geol. u. Paläont., 1913, II, p. 129.

In the space of this book it would lead us too far to go in detail into the countless number of single processes which appear in connexion with Liesegang's rings, and often depend, in a fashion frequently unexplained as yet, upon quite small changes in the experimental arrangement. Instead of the rings similar to the rings of growth of a tree, obtained upon glass plates coated with gelatine, spirals, displacements or breaking-up of the rings into spots, and the like, are observed.[1] Layers of substances which do not directly form rings may be obtained by aid of the pseudomorphous transformation referred to above (p. 735). For instance, a first ring of Ag_2CrO_4 is produced in chromate gelatine by $AgNO_3$ solution, which is then removed and replaced by concentrated $Pb(NO_3)_2$ solution; this diffuses into the gel, transforms the Ag_2CrO_4 into $PbCrO_4$, the $AgNO_3$ set free diffuses further and produces fresh Ag_2CrO_4 rings, which are continually transformed into $PbCrO_4$ rings by the $Pb(NO_3)_2$ following by diffusion. Thus $PbCrO_4$ layers may be formed in gelatine, although such are not formed in it directly by chromate and $Pb(NO_3)_2$.[2]

The manifold variations in Liesegang's rings produced by changes in the experimental conditions have been investigated in detail, since by this means artificial spot and stripe patterns are obtained, which often completely agree with colour patterns occurring in nature.[3] Liesegang[4] has shown that the majority of markings and peculiarities observed in agates may be referred to the formation of such layers. In his "Geologische Diffusionen"[5] he has rendered the same probable for many other geological processes. Gebhardt[6] has considered the patterns on butterflies' wings from this point of view, E. Küster[7] many other colorations. We may mention the stripes on the leaves of *Haborthia fasciata* Haw. and *Aloe variegata* as examples named by Küster.

This mode of explanation must only be applied with great caution. The signs of their mode of production can often only be detected with great difficulty in the stratified structures, and under both geological and biological conditions the possibility of the formation of such layers is great and manifold. Thus R. Goldschmidt[8] has recently shown that the colours on butterflies' wings cannot be explained on the basis of Liesegang's rings. Upon the rings already present in the pupa stage a surface relief of the pattern of the coloured wings is already formed, before the pigments have separated out. The conditions of growth of the wings are therefore the cause of the folds, depressions, and so on, which compose themselves into relief-like patterns, and by which the colours are guided on separating out.

Liesegang,[9] by the way, points out correctly that the nature of the layers hitherto described is only one possibility out of many under which

[1] See e.g. *Liesegang*, Zeitschr. f. physik. Chemie, **88**, 1 (1914); *E. Küster*, "Über Zonenbildung in kolloiden Medien," Jena, 1913; *Hatschek*, Kolloidzeitschr. **27**, 225 (1920).

[2] Experiments by *Hatschek*, Kolloidzeitschr. **14**, 121 (1914); similar experiments earlier by *Liesegang*, Arch. f. Entwickelungsmechanik, **33**, 328 (1911).

[3] See *E. Küster, loc. cit.* under [1]; further *E. Küster*, Kolloidzeitschr. **14**, 307 (1914).

[4] "Die Achate," Dresden and Leipzig, 1915; further Zentralbl. f. Mineral. u. Geol., 1910, p. 593; 1911, p. 497.

[5] *loc. cit.* p. 734.

[6] Verh. d. deutsch. Zool. Ges. **22**, 179 (1912).

[7] *loc. cit.* under [1]; further Die Naturwissenschaften, **2**, 73 (1914).

[8] Arch. f. Entwickelungsmechanik, **47**, 1 (1920).

[9] Zeitschr. f. anorg. Chemie, **48**, 364 (1906); *van Bemmelen*-Festschrift, 1910, p. 33; further *E. Küster*, "Über Zonenbildung in kolloiden Medien," Jena, 1913, p. 12 *et seq.*; Kolloidzeitschr. **12**, 269 (1913).

a rhythmical precipitation may take place. It is always to be expected when the nuclei of the substance thrown down, which are only active as soon as a certain supersaturation is reached or suitable conditions of flocculation have occurred, are isolated in the further course of the process of separation, so that they can no longer act upon the supersaturated solution. This may simply occur upon evaporating a solution in a dish by the separation of solid taking place at the uppermost edge of the liquid, and by the crystal nuclei there formed being later no longer surrounded by liquid owing to the volume of the latter having diminished. A further frequent case consists in the crystals first separated being surrounded by some colloid or other and hence no longer being able to act as crystallization points for the remainder of the supersaturated solution. Upon this depends the stratified structure of such formations as bladder-stones, gall-stones, and others.[1]

It has hitherto always been assumed that one reacting substance is originally distributed uniformly in a gel. It means a fairly fundamental change in the conditions of experiment when both solutions of the reacting substances are allowed to diffuse into the gel from two different sides, say NaCl from one side and $AgNO_3$ from the other. In the middle, as soon as the threshold value is reached, a layer of AgCl separates. If the concentrations of the reacting substances are so chosen that they meet at this point at practically the same velocities, this layer remains thin ; but it soon becomes so dense that all further reaction ceases. If one substance preponderates in concentration and diffusion velocity, the layer grows further in the direction which agrees with the direction of diffusion of the substance which preponderates. The one-sided growth of such layers is a very general rule, pointed out by Pringsheim.[2] It is intelligible, for the substance, diffusing faster and more abundantly, will pass the region of impoverishment in the neighbourhood of the separated layer more quickly and meet in the direction of its diffusion with the second substance in sufficient concentration. The separated layer inhibits diffusion, a circumstance that must also not be neglected in connexion with the Liesegang rings (F. Köhler).[3]

The phenomena become more complicated when a substance such as Ag_2CrO_4 is allowed to separate in gelatine, since it gives Liesegang rings,[4] which AgCl in gelatine does not. In the first place the formation of layers is observed in the region in which the more concentrated solution penetrates into the more dilute. Then the precipitate appears in two different forms : towards the silver nitrate side in a finely disperse red form, on the chromate side in layers, mostly regular, of the crystalline black form. This phenomenon probably depends upon the fact that silver nitrate precipitates Ag_2CrO_4 immediately (cf. p. 737), so that where it is in excess, the Ag_2CrO_4 nuclei rapidly form flakes which separate. In the chromate region, on the other hand, all $AgNO_3$ which penetrates remains dissolved in supersaturation as Ag_2CrO_4, so that the nuclei formed—probably less rapidly than when $AgNO_3$ is in excess—can grow undisturbed to small

[1] *Liesegang*, Kolloidzeitschr. **12**, 269 (1913) ; see particularly also Schade, Kolloidzeitschr. **4**, 175, 261 (1909) ; Münch. med. Wochenschr., 1909, Nr. 1 and 2 ; Kolloidchem. Beihefte **1**, 375 (1910).

[2] Jahrb. f. wiss. Botanik, **28**, 1 (1895) ; *Liesegang*, Naturwiss. Wochenschr. **11**, 353 (1896) ; *Bechhold* and *Ziegler*, Ann. d. Physik (4), **20**, 900 (1906).

[3] *loc. cit.* p. 733.

[4] *Liesegang*, Arch. f. Entwickelungsmechanik, **39**, 362 (1914).

crystals.[1] Foreign substances alter the pattern of red and black Ag_2CrO_4 in a very noteworthy fashion. Thus acids—citric was used—favour the formation of the red form to the disadvantage of the black, so that the latter completely disappears at large concentrations of acid. The acid retains Ag_2CrO_4 in supersaturated solution. Through it the velocity of formation of nuclei—or coagulation velocity—is so much depressed in the chromate region that a separation does not take place there at all, while the $AgNO_3$ throws down Ag_2CrO_4 in the red form, the amount of which is increased by diffusion of supersaturated Ag_2CrO_4 from the region with excess of chromate. The diffusion of this supersaturated Ag_2CrO_4 is so pronounced that red chromate may be deposited contrary to Pringsheim's rule in the direction against the diffusion in excess of chromate. Conversely, we can suppress the formation of the red Ag_2CrO_4 in favour of the black, by working as free from acid as possible and in a concentrated gelatine gel containing gelatose in the right proportion, a behaviour which is still difficult to explain. Liesegang points out how here we get quite definite, sharply characterized forms of deposit, which alter in regular manner with small alterations in the gel and in the reacting solutions. Also in the case of such non-crystalline or very microcrystalline structures we therefore have laws connecting form and material composition, and we get an idea of how the manifold forms of the living world are connected by laws with their material structure.

The Influence of Colloids on the Electrolytic Separation of Metals

It has long been known that colloids influence the electrolytic separation of metals, and technical use is frequently made of it.[2] Now it is very probable that this influence may be referred essentially to the conditions of separation of solid substances in gels. Kohlschütter [3] was the first to put forward this view and to support it by experiments on the electrolytic separation of silver. He electrolysed ammoniacal $AgNO_3$ solutions (0·05 N), which were made slightly alkaline, using Ag electrodes. The silver separated as a fine crystalline powder, which could easily be rubbed off the electrode. With the microscope, one saw small aggregates of metal irregularly distributed over the electrode surface. If a little gelatine was added, the aggregates became smaller and more regularly arranged as the gelatine content increased, until finally a uniform, shining deposit was obtained. A fundamentally similar effect is obtained by the addition of small amounts of other metallic salts, such as copper, zinc, cadmium and magnesium, which can form hydroxides colloidally dispersed in the solution[4] and likewise an addition of copper salt + gelatine or copper salt + starch. The form and distribution of the silver deposit showed sharply

[1] The difference in composition pointed out by *F. Köhler* (p. 734) must also doubtless be taken into account.

[2] See among others *Hübl*, Mitt. d. K. u. K. Militär-Geogr. Inst. **6**, 51 (1886); *Foerster*, Zeitschr. f. Elektrochemie, **5**, 512 (1898); *Senn*, *ibid.* **11**, 233 (1905); *E. Müller* and *Bahntje*, *ibid.* **12**, 317 (1906); *Betts*, "Bleiraffination durch Elektrolyse," Halle, 1910.

[3] *Kohlschütter* and *Schacht*, Zeitschr. f. Elektrochemie, **19**, 172 (1913).

[4] Regarding the presence of colloidal hydroxides in heavy metal solutions see e.g. *Denham* [Zeitschr. f. anorg. Chemie, **57**, 378 (1908); Journ. Chem. Soc. **93**, 41 (1908)].

characterized peculiarities dependent upon the nature and concentration of each salt.

Kohlschütter explains the influence of colloids as follows. The colloidally dissolved substance is adsorbed by the electrode or separated by kataphoresis as a more or less uniform and very fine layer. The electrolytic deposition of a metal does not differ fundamentally from the separation of any kind of difficultly soluble substance from a solution. We have therefore the same series of processes as were described on p. 459; the electric current is the reducing agent which reduces the metallic ion to an uncharged ion. This undergoes a chemical change, for since the charged ion must be regarded as hydrated, it decomposes into a metallic atom and water. Among the metallic atoms set free at the cathode in this way crystal nuclei are formed with a certain velocity, and grow with a definite crystallization velocity to larger crystals. If there is a film of colloid on the cathode, the nuclei are formed in a gel layer, and we have the conditions mentioned above (p. 731). The liquid-solid and uniform nature of the gel favours a uniform separation of the metallic nuclei, and this is the cause of the behaviour just described. To this is added the fact that the colloid is adsorbed on the nuclei and growing crystals, and hence depresses the crystallization velocity in the manner frequently discussed (cf. p. 596); this does not explain the uniform distribution of the separated metal, but certainly the formation of ever finer crystalline masses.

The adsorption of the colloid is only advantageous in that it determines a finely crystalline structure on account of the diminished crystallization velocity. With larger colloid concentrations the adsorption layer may become so thick that the crystals no longer grow together sufficiently; the electrolytic deposit is, it is true, finely crystalline, but loose and powdery. Marc [1] showed this by electrolytic experiments in lead and zinc solutions with addition of various colloids, such as gum arabic and tragacanth. Hence a colloid in itself weakly adsorbable or a substance only capillary-active may be technically more advantageous, because in its presence the precipitate becomes sufficiently finely crystalline, but not loose.[2] Hence we often find it stated in directions that a certain, not too high concentration of colloid is the optimum. It doubtless depends upon this influence that, in Kohlschütter's experiments, a silver solution containing copper salt, which had aged for 15 to 24 hours, did not give a smooth, but a loose and powdery deposit of silver. As the solution ages, too much hydroxide is deposited on the surface of the electrode; it could be seen as an iridescent film upon the electrode. And Sieverts and Wippelmann [3] found that in the electrolytic deposition of copper from $CuSO_4$ solutions, even small additions of colloids render the copper fragile and brittle; the disadvantageous effect upon the strength first becomes noticeable. Only with larger colloid concentrations do we observe a diminution of the copper crystals, and further a stratiform structure.

A large number of facts confirms this view. We find small quantities of the colloid,[4] and of the foreign metals which give colloidal hydroxides, in the metal deposited electrolytically.[5] It is further intelligible that the tran-

[1] Zeitschr. f. Elektrochemie, **19**, 431 (1913); further also *Freundlich* and *J. Fischer*, *ibid.* **18**, 885 (1912).

[2] Thus *Mathers* and *Overmann* [Chem. Ztg. **37**, 341 (1913)] found that for the separation of lead, oil of cloves had a more favourable effect than colloids.

[3] Zeitschr. f. anorg. Chemie, **91**, 1 (1915).

[4] *E. Müller* and *Bahntje*, *loc. cit.* p. 740.

[5] *Kohlschütter* and *Schacht*, *loc. cit.* p. 740.

sition resistance is sensibly increased by the presence of the colloid.[1] Kohlschütter [2] was able to explain from this point of view the well-known smooth deposition of silver and other metals from potassium cyanide solutions. He assumes that in these solutions small amounts of the metallic cyanides are colloidally dispersed, coat the cathode by kataphoresis upon electrolysis taking place, and exert the same influence as the colloids in the experiments described above. That such a coating is formed is confirmed by the following observation. He electrolysed a AgCN solution with a platinum cathode and observed shortly after starting the current a coloured, red-violet to blue-green coating on the cathode, which became silver-white with water or dilute acids. It is obvious that we are dealing with a coat of photohalide, the colloidal mixture of Ag and AgCN, which may be just as well formed in the case of AgCN as of AgCl and AgBr, and also has the properties described (see p. 803).

The colloids do not as a rule alone suffice to guarantee good electrodeposition; the composition of the solution as regards the other anions and kations must fulfil certain definite requirements. Lead, for example, is obtained in a good, firmly adherent coating only from solutions containing hydrofluosilicic acid or chloric acid in the presence of colloids.[3] This will depend, among other things, upon the velocity of formation of nuclei being of a convenient magnitude, and the colloid is not alone sufficient to influence it correctly. It must be recollected that the conditions for an excellent electro-deposit can only occur as the result of a fortunate balance. For good adherence and uniform, finely crystalline formation are, from the start, more or less in contradiction with a good yield at high current densities. With high current densities we have strong supersaturation of the metal at the cathode, and hence with high crystallization velocities the possibility of coarse crystals being formed, with high velocities of formation of nuclei the possibility of loose layers, such as the so-called black silver.[4] All these velocity processes must be correctly adapted to one another if the deposit is to have the required properties. Hence each single case requires separate consideration. It may be mentioned, for instance, that in the electrolytic separation of zinc in acid solution at high current densities, Pring and Tainton [5] observed that colloids not only made the form of the precipitate more finely crystalline and uniform, but also favoured the separation of zinc as compared with hydrogen over a certain range of current densities.

Naturally all these influences produce their effects, when metals separate from their solutions under other circumstances, particularly at a boundary surface. It thus happens that the deposition of silver in the form of a silver mirror is a process which, as Kohlschütter [6] has shown, is governed in a variety of ways by colloido-chemical influences. Under the ultramicroscope the silver mirror resolves itself into a crowd of silver micellæ of amorphous appearance. Hence conditions must be chosen for the formation of the mirror in which the silver separates out in as colloidal a form as possible. As a matter of fact, ammoniacal or weakly alkaline

[1] *H. J. S. Sand* and *Black*, Zeitschr. f. physik. Chemie, **70,** 496 (1910).
[2] Zeitschr. f. Elektrochemie, **19,** 181 (1913).
[3] *Betts, loc. cit.* p. 740.
[4] *Kohlschütter* and *Toropoff*, Zeitschr. f. Elektrochemie, **19,** 161 (1913).
[5] Journ. Chem. Soc. **105,** 710 (1914).
[6] *Kohlschütter* and Frl. *Fischmann*, Lieb. Ann. **387,** 86 (1912).

solutions are always used, since the OH′ ion is an excellent peptizing agent for metallic sols (see p. 509). The OH′-ion content has the further advantage that AgOH, which is strongly adsorbed on glass (see p. 374), is formed in the solution. Since AgOH is more easily and quickly reduced than the complex silver compounds present in the solution, reduction is thus forced to take place in the adsorption layer, that is, at the place where the mirror is required. The reducing agents employed, such as aldehyde, tartaric acid, sugar, and so on, are surface-active. They are adsorbed at the wall, and thus again react, as required, in the adsorption layer; and the resin-like reaction products may cause as thin gel-films a uniform arrangement of the nuclei, and depress the crystallization velocity as protective colloids, as in the electrolytic experiments just considered. The addition to the solution of certain salts, such as those of copper or lead, has been frequently recommended.[1] They are always of the kind which, under the conditions of the experiment, are present in the form of colloidal hydroxides and therefore can likewise influence the process as in the electrolytic separation of silver.

To what extent silver oxide, alkali, small concentrations of electrolyte, reducing agents such as sugar, are favourable to the formation of mirrors, appears from experiments by Lohnstein.[2] If he prepared a colloidal solution of silver oxide by electrolysis of a solution poor in electrolytes and containing sugar, fine mirrors were readily formed upon the glass in the neighbourhood of the electrodes.

As an example of a somewhat different kind, the formation of leaves of metal upon the surface of liquids may be considered. If the cathode in the form of a point or small disc is set just in the surface of a concentrated solution of a metallic salt—solutions of zinc sulphate, chloride, etc., ammoniacal solutions of copper sulphate, silver nitrate, and so on—while the anode lies as a plate opposite to it on the bottom of the vessel, then it is usually observed that the deposited metal does not separate vertically downwards from the point, but spreads out as a thin, shining leaf upon the surface.[3] Here also, in the case of zinc, the behaviour of which has been examined more closely,[4] a whole series of conditions must be fulfilled, as with the formation of a silver mirror. Capillary-active liquids, such as fats, oils, etc., which are spread out at the surface, must be present, doubtless because they wet the metal and hold it floating at the surface, as in the distribution of a powder between two liquid phases (see p. 159). In order to succeed, the separated metal must be finely crystalline and difficultly wetted by water. To this a small quantity of zinc oxide, which is formed in an atmosphere containing oxygen, apparently contributes; in the absence of oxygen the separation of metal on the surface cannot be obtained. This zinc oxide is doubtless, along with the capillary-active substance, the colloid which confers the correct finely crystalline character on the metal, in that by its agency the velocities of formation of nuclei and of crystallization are suitably adjusted. Its amount must not be too great, otherwise growth is completely prevented. Certain foreign substances which influence the velocities of formation of nuclei or of crystallization affect the phenomenon

[1] The copper salt required with many silvering liquids was already made use of by *Liebig* [Lieb. Ann. Suppl. V, 257 (1867)].

[2] Physik. Zeitschr. **10**, 672 (1909).

[3] *Mylius* and *Fromm*, Wied. Ann. **51**, 593 (1894).

[4] *Freundlich* and *Novikow*, Zeitschr. f. Elektrochemie, **16**, 394 (1910).

even in small amounts. $H^{\cdot}$ ions are necessary in a small concentration—perhaps because they peptize the positive colloid, zinc oxide—ammonium ions prevent the formation of a leaf, and allow large crystals to grow vertically into the liquid, perhaps because they oppose the inhibition exerted by the zinc oxide on the velocity of crystallization.

Membranes and Surface Films

Membranes are thin sheets of gel. The important part they play in the economy of living things is well known. Many colloido-chemical phenomena have been directly investigated on membranes and hence discussed earlier; dialysis and ultrafiltration, Donnan's equilibria, and so on. We will now deal in greater detail with the diffusion of dissolved substances through membranes, especially for those membranes which are described as semipermeable. The plasma membranes of cells are membranes of this kind. M. Traube,[1] as is well known, was the first to prepare them artificially, when he showed that many amorphous films, such as are formed by difficultly soluble ferrocyanides, silicates, tannates and so on, are to a large extent semipermeable; they allow water to pass through, but not, or to a much smaller extent, dissolved substances such as sugar, many salts, and the like. Such membranes, as for example those of copper ferrocyanide, are obtained when potassium ferrocyanide acts upon copper sulphate solution, as when the copper ferrocyanide is allowed to separate in the wall of a porous earthenware cell. Membranes of Prussian blue; ferrocyanide of lead, iron, copper; lead silicate; tannate of iron, copper, lead, peptone; are further examples.

In their structure these artificial membranes are not noticeably different from gels. Tinker,[2] who examined them microscopically with an arrangement of the highest possible resolving power, gained, it is true, the impression that the micellæ are coarser than with gels, with diameters between 100 and 1,000 $\mu\mu$. But this is only natural, since the membranes have been produced by the interaction of electrolytes; a coagulation has therefore occurred, which we do not meet with in the sol-gel transformation of gelatine sols. The main point is that the solid micellæ, as in the gel, form the disperse phase, and are separated by micronic to amicronic films of liquid.

Since the membranes are almost entirely to be regarded as concentrated gels, the mechanical influence on diffusion is greatly masked by other influences (see p. 728). It already appears from the earlier investigations of Tammann[3] and Walden,[4] who made comparative tests upon a large number of semipermeable membranes with a series of diffusing substances, that it cannot be a question of a pure sieve action. With a sieve action one should be able to arrange the membranes in a series in the order of their permeability. But this is by no means the case; a membrane particularly impermeable to the majority of substances may be more permeable to some substances than is a membrane which is otherwise, in general, permeable.

Tinker points out that from the probable structure of the membranes alone the conclusion may be drawn that the semipermeability towards truly dissolved substances does not depend upon a purely mechanical

[1] "Gesammelte Abhandlungen," Berlin, 1899, p. 200 *et seq.*
[2] Proc. Roy. Soc., **92**, A, 357 (1916).
[3] Zeitschr. f. physik. Chemie, **10**, 255 (1892).
[4] Zeitschr. f. physik. Chemie, **10**, 699 (1892).

sieve effect. If we assume that three micellæ of equal size touch one another (cf. Fig. 145, *a*), then the radius x of the capillary interspace amounts, as a geometrical calculation shows, to about $\frac{1}{7}$ of the radius r of the micellæ. If the micellæ of the membrane have the diameter given above, we get for x values of from 8 to 80 $\mu\mu$, that is, the capillaries which are the smallest possible in the case of these micellæ are much too wide to hold back, in the manner of a sieve, particles of less than 1 $\mu\mu$ diameter.

Now Fig. 145, *a*, as Tinker remarks, gives by no means a correct picture of the relationships in the membrane. On the contrary, we must distinguish, as has also repeatedly been done in previous discussions (see p. 664), between the liquid belonging to the adsorption layer, and the actual intermicellar liquid. Fig. 145, *b*, in which only the unshaded part corresponds to the actual intermicellar liquid, doubtless gives a picture nearer to the truth. It is at present difficult to give a certain value for the thickness of the adsorption layer (cf. p. 314). Nevertheless we shall not go far wrong with the assumption that with values of x up to 10 $\mu\mu$ the liquid between the micellæ is to be regarded entirely as adsorbed layer, and that therefore, with sizes of the micellæ such as mentioned above, intermicellar

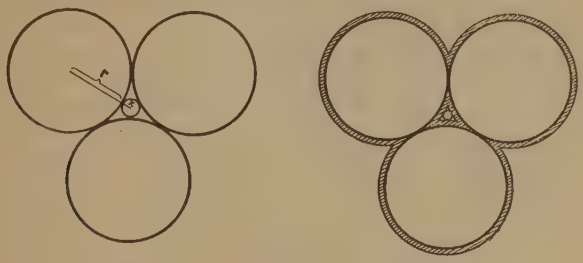


Fig. 145.

liquid with the properties of pure liquid need not be present. This has the consequence, however, that the permeability depends essentially upon the adsorption of the dissolved substances. If they are negatively adsorbed, and this goes so far that the surface layer lying immediately against the micellæ consists practically solely of the pure dispersion medium, this negative adsorption may become the cause of the semipermeability; an idea first discussed by Nathansohn[1] and independently by Tinker. As long as the capillary interspaces are so fine that practically no intermicellar liquid is present, but only adsorbed water, the dissolved substance does not pass through. In actual fact the membranes are semipermeable in the first place for salts, and then for substances such as sugar and the like, the negative adsorption of which is known (cf. p. 688). The wider the capillary interspaces become, and the larger therefore the intermicellar liquid canals, the less semipermeable does the membrane become. According to Tinker, the fineness of the pores of various membranes actually runs parallel with their semipermeability, although, which at first appears curious, the pores in themselves are too wide to exert a direct sieve action. Thus Tinker found the finest micellæ, and accordingly the finest pores, in membranes of copper ferrocyanide and ferric ferrocyanide, coarser in membranes of silicates and tannates of the heavy metals, and the coarsest

[1] Jahrb. f. wiss. Botanik, **40**, 431 (1904).

with peptone tannate; and according to M. Traube, the same order holds for their semipermeability.

A fact discovered by Bartell [1] accords well with this view. Membranes, such as say those of unglazed porcelain, which are known to be completely permeable, become sensibly semipermeable, give, therefore, an osmotic pressure, for instance, against sugar solutions, when the pores are very fine, or when the coarser pores are diminished in size by stopping up with suitable precipitates, such as $BaSO_4$, $PbCO_3$, CuS, etc. He determined the diameter of the pores by determining the pressure necessary to force air through the membrane against water, that is to force the water out of the pores. This pressure is equal to the height to which water would rise in the capillaries of the membrane on account of the surface tension. It now appeared that it was really a matter of the diameter of the pores. Osmotic effects against sugar solutions do not occur when 65 to 80 pores go to the sq. cm. of the membrane, with a diameter of the single pore of more than $0{\cdot}9\mu$; below this they appear fairly independently of the nature of the precipitate filling the pores.

As regards the semipermeability of the plasma membranes of the cells towards salts, sugar, and so on, it is by no means so definite that we are able to say that under all circumstances only water passes through, but not the substances named. This is the case when pure water or a not too concentrated solution is outside. If there is a more concentrated solution outside, salts or sugar pass through. This is recognized by the fact that the cells plasmolyse in the solution, but the longer the time during which they are in the solution, the higher the external concentration of salt necessary to produce a certain degree of plasmolysis. Thus Troendle [2] was obliged, when he desired to obtain the same degree of plasmolysis in experiments on the root cells of *Lupinus albus*, to raise the external concentration of KCl from 0·437 molar to 2·488 molar, when the cells remained 40 minutes instead of 2 minutes in the solution. This is to be explained by salts penetrating into the cells, and hence rendering it necessary to raise the external concentration if liquid is to pass from the interior to the exterior of the cell.[3]

From the rate at which the external concentration must be increased we may deduce the rate at which the salt penetrates. It remains at first constant, and decreases later, and is found *not* to be controlled by the difference between the concentrations in the interior and exterior. Troendle concludes correctly that it is not due to a diffusion effect, and assumes in place of it biological changes in the protoplasm. In my opinion it should first be tested whether we are not dealing with an osmosis due to swelling processes such as are discussed on p. 697; in this case a connexion with the rate of swelling would be expected, and it would likewise not require to stand in any simple relation to the difference in concentration. The idea is the more plausible, since in these experiments of Troendle's, as in swelling processes, the lyotropic series of the ions is plainly felt. The rate

[1] Journ. Phys. Chem. **16**, 318 (1912).

[2] Arch. d. Science phys. et natur. (4), **45**, 38, 117 (1918).

[3] The penetration of electrolyte into the interior of the cell follows also from experiments by *v. Moellendorff* [Kolloidzeitschr. **23**, 158 (1918)]. An acid dye (trypan blue), which had penetrated into the liver and suprarenal cells of tadpoles could be coagulated in these cells by allowing salt solutions to act upon them; the valency of the kations showed its effect.

of penetration of the salt increases greatly in the case of chlorides in the kation series

$$Li < Na < K < Rb.$$

The $Li^{\cdot}$ ion penetrates most slowly, the $Rb^{\cdot}$ ion most rapidly. This is in contradiction with the size of the atoms, but entirely corresponds to their affinity for water, Li having the greatest, Rb the smallest. Quite in agreement is the series of the anions, which for the Na salts runs

$$SO_4 < Cl < NO_3 < Br,I.$$

From the direction of the osmosis we should conclude that the colloids, upon whose swelling it depends, swell more slowly in the salt solution than in the cell-liquid.

In any case, the conditions of swelling and the swelling velocity of the colloids in question change in such experiments as the swelling in such salt solutions proceeds. Hence it comes about that when during these measurements the concentration of the external liquid is not increased, but the cells are left in the same solution, the plasmolysis at first appearing decreases more and more, until it finally stops.[1] The end state does not, however, consist in equal concentration ruling inside and out. This doubtless depends upon the conditions of permeability of the plasma membrane having changed as a result of swelling. On the other hand, in the case of salts, Donnan membrane equilibria may play a part. For the interior of the cell is unquestionably rich in colloid electrolytes.[2]

For a large number of substances such as the alcohols, urethanes, and so on, the plasma membranes are permeable. Between this permeability and the solubility of the substances mentioned in fats and fat-like substances there exists a distinct parallelism. This fact led to the well-known "Lipoid" theory of Overton [3] and H. H. Meyer,[4] according to which the plasma membrane consists essentially of lipoids; the fact that these substances preferentially dissolve alcohols, urethanes, and so on, would suffice to explain the permeability for such substances. When later a series of facts to be discussed immediately made the lipoid theory untenable in this form, it was sometimes [5] assumed that the plasma membrane is a mosaic of protein and lipoid micellæ, and the simultaneous permeability for water and for substances soluble in fats was interpreted on this basis. This view does not appear to be necessary, however. I. Traube [6] pointed out that the

[1] *Fitting*, Jahrb. f. wiss. Bot. **56**, 1 (1915).

[2] That it is not a matter of electro-osmotic effects appears to follow from the fact that according to *Collander* [Pflüg. Arch. **185**, 224 (1920)] ions of high valency which are so active electrokinetically are without influence on plasmolysis.

[3] Vierteljahrsschr. d. Naturforsch. Ges. in Zürich, **40**, 1 (1895); **44**, 88 (1899).

[4] Arch. f. exper. Pathol. **42**, 109 (1899).

[5] *Nathansohn*, Jahrb. f. wiss. Botanik, **39**, 638 *et seq.* (1904); see also *Czapek*, Internat. Zeitschr. f. phys.-chem. Biol. **1**, 108 (1914).

[6] Pflüg. Archiv, **105**, 54 (1904); Ber. d. deutsch. physik. Ges. **6**, 326 (1904). Since then a large number of biological phenomena have become known for which *Traube's* rule has been shown to hold. Thus the exosmosis of many constituents from the cells first commences when the surface tension of the aqueous solution of a foreign substance, in which the cells are placed, has reached a certain small value [*Fühner* and *Neubauer*, Arch. f. exper. Pathol. u. Pharmakol. **56**, 333 (1907); *Czapek*, "Über eine Methode zur direkten Bestimmung der Oberflächenspannung der Plasmahaut von Pflanzenzellen," Jena, 1911; *Kisch*, Biochem. Zeitschr. **40**, 152 (1912); on the other hand *Vernon*, Biochem. Zeitschr. **51**, 1 (1913)]. Fundamentally, it doubtless depends upon the change in the interfacial tension, which in these cases goes parallel with the surface tension. Since this characteristic value of the interfacial tension is reached

lipoid solubility is to a great extent symbatic with the adsorbability obeying his rule, and indeed, substances must pass through a membrane according to their adsorbability, if, for example, as in the cases above considered (p. 745), no intermicellar liquid is present and the adsorbed solute displaces water molecules from the adsorption envelope. That adsorbability and lipoid solubility may run parallel, is not remarkable; adsorbability in aqueous solution is an expression of a sensibly hydrophobic character, and hydrophobic substances are also often decidedly soluble in oils and fats.

The facts which contradict the lipoid theory so decisively are the observations of Ruhland [1] on the taking up of dyes by plant-cells. He found that this is symbatic with the power of dyes of diffusing into gelatine gels; the truly dissolved dyes diffuse rapidly, and also penetrate quickly into plants, while dyes the solutions of which are increasingly colloidal also diffuse and penetrate increasingly more slowly. This has quite the appearance of being a mechanical sieve action, as in the case of ultrafiltration, and an effect of this kind is not excluded, since the micellæ of the dye solutions may very well approach in diameter the diameter of the submicronic membrane pores. For we certainly have reasons for assuming that the micellæ, and hence also the pores of these plasma membranes, are smaller than those of the artificial semipermeable membranes mentioned above (p. 744). Also in those cases where the pores are so fine that the liquid filling them may be regarded as almost entirely adsorbed, the passage of small molecules of dye—assuming that they are only positively and not decidedly negatively adsorbed—will be rendered easier. From these experiments there was found in the first place a series of dyes, such as methylene green, thionine, malachite green, methyl green, azophosphine G.O., and new blue R, which, since they diffuse well, also penetrate rapidly into the cells, although they are insoluble in lipoids; that is to say, they dissolve but feebly in olive oil or in a solution of cholesterol in turpentine. Conversely, some dyes which do not penetrate or diffuse, such as night blue, Victoria blue B and R, Basel blue, are easily soluble in solutions of cholesterol in benzene or cholesterol in turpentine, as the case may be. Hence they do not penetrate in spite of their solubility in lipoids. In my opinion this behaviour tells definitely against the lipoid theory.

Schumann [2] arrived at results which quite corresponded with these in the case of the vital staining of animals by acid dyes. The smaller the dye molecules and the more easily they dialyse, the more rapidly are animal tissues saturated, the more rapidly also is the dye excreted again by the animal. Dyes whose solutions are colloidal do not diffuse but remain at the place at which they are introduced.

with capillary-active substances at correspondingly smaller concentrations, *Traube's* rule holds for them. That the narcotic action obeys it, is obvious when we consider that the alcohols, urethanes, etc., whose power of pasing through the membrane called the lipoid theory into being, are compounds with distinct narcotic action [see also *J. Loeb*, Biochem. Zeitschr. **23**, 93 (1909); Fühner, Zeitschr. f. Biologie, **57**, 465 (1912); Frau *Nothmann-Zuckerkandl*, Biochem. Zeitschr. **45**, 412 (1916); *Veszi*, Pflüg. Arch. **170**, 313 (1918), and others].

Moreover, the concentrations of the primary alcohols with which a sensation of smell or taste first appears can be arranged according to *Traube's* rule [*Hallenberg*, Skand. Arch. f. Physiol. **31**, 75 (1914)].

[1] Jahrb. f. wiss. Botanik. **46**, 1 (1908); **51**, 376 (1912); Ber. d. deutsch. bot. Ges. **26a**, 772 (1908); further also *Höber* and Frl. *Kempner*, Biochem. Zeitschr. **11**, 105 (1908); *Höber, ibid.* **20**, 56 (1909); *Höber* and *Nast, ibid.* **50**, 418 (1913); *Höber, ibid.* **67**, 420 (1914).

[2] Biochem. Zeitschr. **80**, 1 (1917).

The permeability of membranes is however only one circumstance of importance for vital staining. Bethe [1] pointed out that it alone cannot be decisive, since otherwise we could not understand why many easily diffusible acid dyes do not stain, while easily diffusible basic dyes do so. In his opinion this depends upon the further circumstance whether the cells store up the dye, which means, doubtless, whether they adsorb it or not. Only if the dye is in any way bound in the cells does the power of passing into the membrane take effect and permit of detection. In accordance with the general rule (cf. p. 209), Bethe was able to show that cells which have a weakly acid reaction in their interior store up basic dyes, and are vitally stained by them, while those which have a basic reaction behave in a corresponding manner towards acid dyes.

Of the passage of solutes through membranes we will discuss a further example, which perhaps concerns but little the membranes usually occurring, since they are too thin, but is of fundamental importance.[2] It is true that the example relates to a liquid layer of separation, but the transference to gel-like solids appears quite permissible. If a gelatine gel stained with methylene blue be covered with a thin layer of chloroform, and the chloroform with water, the dye does not penetrate through to the water, since it is insoluble in chloroform. If the chloroform is replaced by a solution of spermaceti in chloroform, the methylene blue migrates comparatively rapidly through to the water, since the spermaceti micellæ [3] contained in the chloroform adsorb dyes and give them up again in part to water; the solution of spermaceti in chloroform is but feebly coloured blue in the process. If instead of the spermaceti solution a spermaceti milk (see p. 656) is taken, which adsorbs methylene blue strongly, the intermediate layer appears deep blue; the water, on the other hand, is coloured much less quickly than in the former case. This depends upon the fact that the methylene blue is held back in quantity in the intermediate layer precisely on account of the strong adsorption; hence it would have to be supplied much more quickly and abundantly from the gelatine gel than is actually the case, if a rapid coloration of the water is to be produced. A strong adsorption in the intermediate layer is therefore sometimes not most advantageous for a rapid penetration by the diffusing substance.

It has been frequently pointed out how solid films of gel may be formed on the surface of colloidal solutions, as in the case of the sols of proteins,[4] peptone,[5] many dyes,[6] Paal's metal sols [7] containing protective colloids, and others. The skin formed on boiled milk is an everyday example of this phenomenon. The first stage in time of this effect is undoubtedly an adsorption on the surface. This does not suffice to explain all properties of the films, such as their solidity and insolubility in the dispersion media from which they are formed. One must assume in the

[1] Wien. Med. Wochenschr., 1916, Nr. 14; further *K. Rohde*, Pflüg. Archiv, **168**, 411 (1917).

[2] *S. Loewe*, Biochem. Zeitschr. **42**, 181 (1912); *Freundlich* and *Gann*, Internat. Zeitschr. f. phys.-chem. Biologie, **2**, 14 *et seq.* (1915).

[3] We have every reason to assume that the slight solubility of the dye in the spermaceti solution depends upon a small number of micellæ being formed on account of an impurity in the spermaceti (see p. 656).

[4] See *Ramsden, loc. cit.* p. 535.

[5] See *Metcalf, loc. cit.* p. 535.

[6] See *O. Rohde, loc. cit.* p. 282.

[7] See *Plogmeier*, Verh. d. deutsch. physik. Ges. **11**, 393 *et seq.* (1909).

first place that the micellæ tightly packed in the surface coagulate, and in the case of protein and allied substances they are chemically altered, denatured. The increased concentration in the surface and the consequent formation of such films may be reached both from low and from high concentrations. They arise in the first place in sols in which the micellæ were originally quite uniformly distributed. Then they may also be formed by allowing, for instance, a small amount of a concentrated solution to drop upon water, as has been particularly investigated in the case of peptone; on account of the lower surface tension the solution spreads out upon the water surface (see p. 96) and may solidify rapidly to a film under suitable conditions. The amount brought upon the surface may be larger than that required to form the film, whereupon peptone subsequently diffuses away from the film into the water.

The solidity of such films, the so-called surface solidity, is a property which may be readily followed. For this purpose a disc of glass is allowed to oscillate in the surface. If the surface does not differ sensibly from the interior, the oscillations are damped just as strongly in the surface as in the interior. If a film of a certain strength is present, the torsion head, to which the disc is attached by a fine wire, must be turned through a certain angle before the disc follows. This angle φ is a measure of the strength of the film. Schütt [1] was the first to carry out measurements in this manner, after Plateau [2] had already observed that in many liquids, particularly colloidal solutions, an oscillating magnetic needle is more strongly damped on the surface than in the interior. From the oscillations of such a needle-shaped body no definite conclusions can be drawn, for every contamination of the surface with a capillary-active substance, and not only a solid film, must exercise a damping effect of this kind. When the needle swings the capillary-active substance is pushed together in front of the needle, behind it there remains a pure surface of high tension. The liquid moves from places of lower surface tension to those of higher; hence around the point of the needle in a direction opposed to its motion, and hence damps the latter. An oscillating disc, on the other hand, leads to correct results.

Such films are given by colloidal solutions, such as those of the proteins, and by semi-colloidal solutions, such as those of the peptones, dyes, etc. If they are formed in true solutions, it is probable that they are composed of substances which have been formed in colloidal dispersion from the true solutes. Thus Nagel [3] obtained films upon a concentrated solution of cobaltic chloride; here it could be definitely proved that they consisted of a basic cobaltic carbonate, the presence of which was due to the action of small amounts of ammonium carbonate present as an impurity. Oxygen has nothing to do with the formation of films upon protein, peptone, and dye solutions; only in the case of mercury does a surface solidity sometimes appearing depend on an oxidation.[4] Evaporation hastens the formation of the film, but is not its cause; it also takes place in a space completely saturated with vapour.

O. Rohde [5] followed the time-course of the increase in solidity in dye-solutions. The surface of a concentrated fuchsine solution, for instance, is at first quite mobile. A piece of cork on the surface follows every touch.

[1] Ann. d. Physik (4), **13**, 712 (1904).
[2] "Statique des Liquides," **2**, p. 261 *et seq.*, Paris, 1873.
[3] Ann. d. Physik (4), **29**, 1041 *et seq.* (1909).
[4] See *Schütt, loc. cit.* under [1].
[5] *loc. cit.* p. 282.

A disc is damped to exactly the same degree at the surface as in the interior of the liquid. Already in course of the first hour the surface changes in appearance. Instead of being brightly reflecting, it becomes duller, greyer, and finally acquires a green tinge ; a piece of cork no longer follows every touch, and by means of an oscillating disc a definite solidity can be measured in the manner described. In Fig. 146 the times t in hours are plotted as abscissæ, and as ordinates the angle φ, which is a measure of the solidity of the skin. These curves have a pronounced auto-catalytic character. Since this is found both in the case of coagulation and in the coarsening of coagulated particles (see p. 454), it is probable that here also coagulation or coarsening is the cause of this time-course, while the actual adsorption proceeds comparatively rapidly [1] (but cf. p. 535). This does not mean that this course is peculiar to coagulation or coarsening. It may also be caused by a subsidiary circumstance (see p. 437). In agreement with this view is the fact that electrolytes, in accordance with their coagulating action,

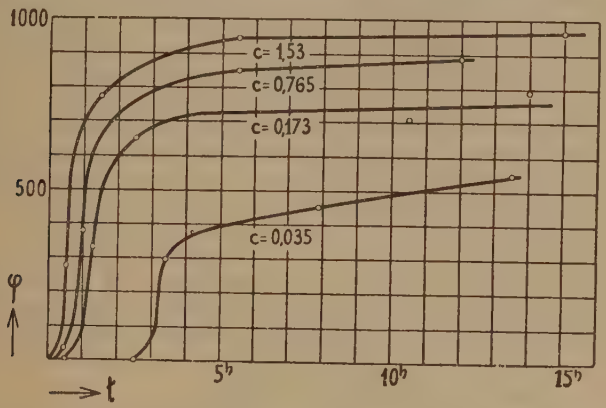


Fig. 146.—Rate of Formation of Film upon the Surface of Fuchsine Solutions.

greatly accelerate the formation of films upon dye solutions and metal sols ; and in the case of a negative palladium sol the influence of the valency of the kations again appears.[2]

We see further from Fig. 146 that the end state to which every solution tends depends upon the concentration. If we regard the solidity attained in equilibrium as a measure of the amount adsorbed on the surface, which is permissible as a first approximation, it appears that the amount adsorbed obeys the ordinary adsorption isothermal in its dependence upon the concentration in the solution.[3]

Parallel to the increase in strength of the films we have an increase in the sensitivity of the surface to light, if the solid which separates as a film is photoelectrically sensitive. In contradiction to O. Rohde, Plogmeier [4] found that the photoelectrical sensitivity is not strictly symbatic with the formation of the film. This may be the reason why the results of Plogmeier,

[1] In favour of this is the fact that the motion of camphor particles on water is immediately stopped by ethyl green [*Liesegang*, Kolloidzeitschr. **3**, 228 (1908)].

[2] *Plogmeier, loc. cit.* p. 749.

[3] See " Kapillarchemie " (1st Ed. of this book), 1909, pp. 79, 80.

[4] Verh. d. deutsch. physik. Ges. **11**, 382 (1909).

who only investigated the surface as regards its photoelectric behaviour, differed from those of Rohde as regards the dependence of the end state upon the dye concentration, and as to the nature of the time-course. To this must be added the fact that dyes are frequently not very pure, and that it is therefore uncertain if the two workers were dealing with precisely the same substance. In agreement with the adsorption theory of solid films we have the fact that such films are only formed in aqueous dye solutions, in which the dyes are colloidally dissolved, reduce the surface tension, and consequently are adsorbed. In alcoholic solutions, in which this is not the case, no film formation is observed.[1]

Metcalf [2] particularly examined peptone films on water surfaces, prepared in the way described above, by allowing a few drops of a peptone solution to spread over a water surface. The strength of such films passes in course of time through a minimum, which is explained by the fact that along with the gradual solidification, the diffusion of the peptone from the surface into the solution is a process which diminishes the amount of substance collected at the surface, and therefore the strength of the skin.

The formation of films on surfaces and at interfaces unquestionably plays an eminent part in the phenomena of life, particularly in cell division and growth. These processes have not yet been so analysed into their separate steps as to abolish the danger of deception by a superficial similarity. Nevertheless it is worthy of note that just as in coagulation, coarsening, and film formation, so in many processes of growth we have, according to Wo. Ostwald,[3] Brailsford Robertson,[4] and others, a very pronounced autocatalytic time-course.

A process which depends both upon the formation of films and upon the semipermeability of the resulting membranes is the so-called artificial plant-growth in the test-tube, which is noteworthy not only on account of its external similarity with living structures, but also because it must be taken into account in various natural processes.

M. Traube [5] was one of the first to describe it in connexion with his investigations of semipermeable membranes; Quincke,[6] Leduc,[7] Lüppo-Cramer,[8] Liesegang,[9] B. Moore,[10] and others have then taken up its investigation from various points of view.

The phenomenon is as follows. If a crystal, for instance of manganous chloride, be laid upon the bottom of a vessel filled with a waterglass solution of suitable concentration, thread-like tubes grow upwards out of the crystal; they radiate branches sideways, which again fork into fine twigs, so that finally a plant- or moss-like structure fills the whole test-tube. The

[1] *O. Rohde, loc. cit.* p. 282.

[2] *loc. cit.* p. 535.

[3] "Vorträge und Aufsätze über Entwicklungsmechanik der Organismen," Heft V, 1908.

[4] Arch. f. Entwicklungsmechanik, **25**, 581 (1908); **26**, 106 (1908); see also *Backmann* and *Runnström*, Pflüg. Archiv, **144**, 287 (1912).

[5] "Gesammelte Abhandl.," Berlin, 1899, p. 200 *et seq.*; above all pp. 275–6.

[6] Among other places Ann. d. Physik (4), **7**, 640 (1902); **11**, 449 (1903).

[7] Compt. rend. **144**, 39 (1907); further *Leduc*, "La Biologie Synthétique," Paris, 1912.

[8] Kolloidzeitschr. **9**, 116 (1911).

[9] Geolog. Rundschau, **5**, 241 (1914); Kolloidzeitschr. **9**, 298 (1911); **15**, 18 (1914); "Die Achate," Dresden and Leipzig, 1915, p. 55 *et seq.*

[10] *B. Moore* and *Evans*, Proc. Roy. Soc. **89**, B, 17 (1914); *B. Moore, ibid.* **89**, B, 27 (1914).

crystal dissolves, the dissolved $MnCl_2$ reacts with the silicate, and thus close around the crystal a film of manganese silicate is formed. This is, as already mentioned concerning other heavy metal silicates (see p. 744), semipermeable; water can pass through, but not sodium silicate. The membrane thus surrounds as in a cell the $MnCl_2$ solution surrounding the crystal. It is stretched more and more by the water which penetrates into it, until at a particularly weak point a jet of manganous salt solution is spurted out of the interior of the cell into the silicate solution. This jet is quickly surrounded by a film of manganous silicate, and the same process is repeated with it. The upward direction of growth is caused by the film always being thinnest at the top, and hence giving way there. The thinnest part is at the top, since the specifically lightest, hence most dilute, part of the liquid collects there. The properties of the ions present make themselves felt in various ways, especially for the reason that the properties of the gel film depend upon them; thus when manganous sulphate is used the vegetation does not develop nearly so richly, doubtless because the envelope is much more rigid and less permeable. It is probable that the formation of so-called moss agates depends upon artificial vegetation of this kind, very similar structures being obtained by allowing waterglass solution to act upon a crystal of ferrous sulphate. Gergens [1] had already given this explanation in 1858 and reproduced the phenomenon in a test-tube, and Liesegang [2] repeated it independently.

Periodical chemical phenomena of quite a different kind have been connected with the appearance and disappearance of films upon surfaces. Thus according to the investigations of Bredig and his co-workers,[3] the decomposition of H_2O_2 at a mercury surface assumes a periodic character with a suitable OH'-ion concentration, the phenomenon depending upon the ever-repeated production of a golden yellow film upon the mercury, probably consisting of a mercurous salt of H_2O_2, a mercurous peroxidate.[4]

Dyeing, Tanning, and Related Processes[5]

In the course of this description the strong adsorption of dyes by the most diverse adsorbents has repeatedly been referred to, and has been used as an example for various regularities. Here we will go more into detail concerning technical dyeing and the adsorption of dyes by proteins and the like.

It is only a question of time for the view to be generally recognized as correct that there is no general theory of dyeing, but that in every dyeing process several processes are superimposed, which may differ according to the nature of the fibres and of the dye solution.[6] We may very generally assume that the first stage in point of time of every dyeing process is an adsorption of the dye, but only rarely will the fibres be truly dyed as a consequence of this process. But even then colloido-chemical processes frequently suffice for explanation.

[1] Neues Jahrb. f. Mineralogie, 1858, p. 801.

[2] *loc. cit.* p. 752.

[3] *Bredig* and *Weinmayr*, Zeitschr. physik. Chem. **42**, 601 (1903); *Bredig*, Biochem. Zeitschr. **6**, 322 (1907); *v. Antropoff*, Zeitschr. physik. Chem. **62**, 513 (1908).

[4] *v. Antropoff*, Journ. f. prakt. Chem. **77**, 273 (1908); *Bredig*, Zeitschr. f. Elektrochem. **12**, 585 (1906).

[5] Recent books in English are "A Manual of Dyeing," *Knecht Rawson* and *Lowenthal*, 2 V., London, 1916; "Application of Dye-Stuffs," *Matthews*, London, 1920. These are purely practical treatises. See also *King*, I.B.A. Rep. on Coll. Ch., p. 20.

[6] See *Haller* and *Nowak*, Kolloidchem. Beihefte **13**, 61 (1920).

The dyeing of *cotton* has been to a large extent elucidated, especially by the recent investigations of Haller.[1] It has long been known that cotton differs essentially as regards its dyeing qualities from the animal fibres silk and wool. This depends in the first place upon the fact that cotton is distinctly crystalline (see p. 725) and in accordance with a common rule, the adsorptive power of crystalline substances is less than that of amorphous. To this is added the fact that in accordance with its chemical constitution it is unable or scarcely able to adsorb by exchange, or to form salts. It was remarked earlier (p. 213) that the possible exchange adsorption observed with filter paper is to be referred to the presence of ashy residues. Hence it is natural that a group of substances so generally strongly adsorbed as the basic dyes, dye cotton but little and not fast without special pre-treatment and methods. But, as is well known, there is another group of dyes, the *substantive cotton dyes*, which have a very pronounced power of dyeing cotton under fairly simple conditions. They are salts of the carboxylic and sulphonic acids of tetrazo- and polyazo-compounds; the Congo dyes, benzopurpurine, benzazurine, and others, belong to this group. Their solutions are found to be throughout colloidal or semicolloidal. The adsorption of the dye follows the usual isothermal.[2] According to Haller, microscopical and ultramicroscopical tests, which may be further improved by allowing the fibres to swell and dissolve in cuprammonium solution, give the following results. The dye is located almost entirely upon the outer layer of the fibres, but not completely upon the surface, having penetrated into it a little; but comparatively little dye penetrates to a great depth. It depends therefore upon an external and not on an internal surface of the fibres. It seems, as Haller points out, as if a quite definite size of micella were necessary [3] in order for it to be held fast in this way upon the surface of the fibres. If they are too fine and amicronic, they penetrate into the interior of the fibres, but the dye is not fast. If they are too coarse, under the dyeing conditions (boiling the dye bath with additions of salts) coagulation takes place in the solution, which is likewise disadvantageous to dyeing. The addition of salt is to bring as much as possible of the dye into the degree of dispersity which causes sufficiently fast dyeing.

Basic dyes may be used to dye cotton when mordants are employed. Tannin, the solution of which is semi-colloidal but apparently so finely disperse that it completely penetrates the fibres and is reversibly adsorbed by them, may be used as a mordant. In order to hold it fast to the fibres, it is transformed by treatment with a suitable salt solution, generally one of antimony, into a difficultly soluble metallic tannate, and the fibres thus mordanted are dyed with basic dyes. Haller assumes an actual chemical compound between tannin and basic dye; the degree of dispersity of the tannin solution decreases very greatly upon addition of basic dyes, as may be recognized ultramicroscopically, and also from the fact that the solution no longer dialyses through dialysis thimbles. This might also be referred to an adsorption. Perhaps the simultaneous appearance of the shift in the

[1] Chem.-Ztg. **36**, 169, 182 (1912); Kolloidzeitschr. **11**, 110 (1912); **13**, 255 (1913); **20**, 127 (1917); **23**, 100 (1918); Färberztg. **23**, 489, 523 (1912); **24**, 227, 257, 282, 305 (1913); **25**, 301, 321 (1914); *Haller* and *Nowak, loc. cit.* p. 753.

[2] *W. Biltz, loc. cit.* p. 481. The same is true of the sulphur dyes and their solutions [*W. Biltz*, Ber. d. deutsch. chem. Ges. **38**, 2973 (1905)].

[3] Perhaps a definite form of the particles is also important. For these sols are able to a striking degree (see p. 414) to give upon addition of electrolyte rod-shaped particles and doubly refracting sols.

adsorption band speaks more in favour of a chemical compound, although of course changes in the degree of dispersity may also be connected with strong colour changes (see p. 652). The dyeing of the mordanted fibres therefore depends upon the fact that the basic dyes are adsorbed by the tannin compounds present in the fibres, or chemically combined to them.

It would lead us too far to discuss the manifold, mostly colloido-chemical processes, to which, according to Haller, dyeing with alizarin, aniline black, and so on, is to be referred.

Silk and *wool* are, as compared with cotton, much less crystalline ; wool, indeed, unmistakably amorphous (see p. 725). In accordance with this fact are their far greater adsorptive powers, which extend to a far greater number of substances, thus to the basic dyes, alkaloids, corrosive sublimate, etc. With the more amorphous structure of these fibres an adsorption on the inner surface of the micellæ doubtless comes into question more frequently than in the case of cotton. It has much more frequently the character of an exchange adsorption, since both silk and wool as proteins are colloidal electrolytes (cf. p. 569). It has already been shown (p. 236) that the actual formation of a salt must be separated from a quick adsorption, and that it takes place gradually. It may be due to this, if difficultly soluble salts are formed, that the adsorption is not reversible, and the dye therefore fast. But it is an open question whether this formation of salt is the only chemical process which we must take into account, and which conditions the fastness of the colour. Polymerization appears to occur frequently in adsorbed layers of dyes ; we may recollect how the films separating on the surface of an aqueous dye solution were frequently difficultly soluble (see p. 750). Processes of this kind must also be assumed to be possible. But a very considerable coarsening does not appear to take place in the fibres. Haller [1] made extensive series of experiments, not only with dyed fibres, but also with other dyed adsorbents (mixtures of palmitic and stearic acids and so on), with which he dissolved away the adsorbent by suitable solvents and examined ultramicroscopically the form in which the dyes remained behind. Mainly amicronic and submicronic particles appear to occur, not coarse microns.

It is true that much tells in favour of the necessity of taking into account exchange adsorption, and hence the important opposite charge of adsorbent and adsorbed substance, to a pre-eminent degree, especially also in the case of the influence of foreign substances such as acids, bases, and salts upon dyeing. This has been pointed out especially by Pelet-Jolivet.[2] This is intelligible when we recollect the amphoteric behaviour of the proteins, and the ease with which they reverse their charges. Acids produce colloidal kations, increase an already existing positive charge, diminish a negative one, and possibly lead to a reversal to positive. They further set the acid free from an acid dye salt. These circumstances are united in the sense that they favour dyeing with acid dyes, and affect adversely that with basic. Bases act in the opposite manner, favour dyeing with basic dyes, and oppose that with acid ones. In agreement with this behaviour is the action of ions of high valency ; multivalent kations assist dyeing with acid dyes, multivalent anions that with basic dyes. Pelet-Jolivet [3] points out how similar is the influence upon the capillary rise of the dyes. It is here'

[1] Kolloidzeitschr. **22**, 113 (1918) ; **27**, 30 (1920).

[2] "Die Theorien des Färbeprozesses," Dresden, 1910.

[3] *Pelet-Jolivet* and *Jess*, Kolloidzeitschr. **3**, 275 (1908) ; *Pelet-Jolivet, ibid.* **5**, 238 (1909).

as in many similar cases, difficult to decide whether it is more a matter of a direct change in the charge which conditions the electrokinetic processes, or of the coagulation so closely connected with them. Indeed, as in the case of coagulation, oppositely charged dye and fibre micellæ might meet and associate to more closely linked complexes.

It may be remarked that the contrast between crystalline cellulose and amorphous wool is also evident in the fact that ramie fibres (cellulose), when dyed with many and various dyes (cotton dyes and also basic), show strong dichroism.[1] On the other hand wool shows no dichroism or only a feeble one with either acid, basic or direct cotton dyes. This will be explained by the molecules of dye taken up in the fibres which have crystalline micellæ being orientated, those in the amorphous fibres little or not at all.

Regarding the fastness of dyeing, it may be remarked that as a rule special circumstances, such as chemical interactions and the formation of insoluble compounds, will doubtless be responsible for it. But we may point out here as well (cf. p. 193) that if the dye bath is exhausted by dyeing, the colour will necessarily not allow itself to be visibly washed out by water; for the concentration of the dye in the wash water can only be smaller than in that solution which originally was in equilibrium with the dyed fibres during the dyeing process.

In the staining of cell constituents, so successfully made use of in microscopic technique, we meet, as is to be expected, with phenomena similar to those in the dyeing of wool and silk. The contrast between acidophilic (or basophobic) and basophilic (or acidophobic) structures [2] is none other than that between positive and negative adsorbents, of which the first preferentially or solely adsorb acid dyes, and the latter basic. This also corresponds to numerous other experimental results (see p. 209) in which the tendency to take up basic dyes is more pronounced than the preference for acid dyes. There are substances such as the nucleic acids, and in a lesser degree also the nucleins, which are one-sidedly acidophobic, and hence only dye with basic dyes; on the other hand no one-sidedly basophobic structures are known.

Also the particular staining character of certain dyes towards cells frequently agrees well with their properties otherwise observed as regards adsorption. Thus *methyl green* is a dye which is in general weakly adsorbed, is hence easily washed out,[3] and is taken up preferentially only by the most negative, that is, acid adsorbents; while it therefore stains many proteins, such as albumin and globulin, but little, it is decidedly adsorbed by nucleic acids and nucleins.[4] Quite generally, methyl green is only weakly adsorbed; with such different adsorbents as the negative bole, the positive fibrous alumina, and the fairly neutral blood charcoal, it occupies, as a weakly adsorbable dye, the last or the penultimate position in the following series of dyes: chrysoidine, malachite green, auramine, safranine, new fuchsine, methylene blue, methyl green.[5] The peculiarity of methyl

[1] *Fox*, "Beiträge zur Kenntnis der Färbeforgänge," Diss., Jena, 1908.

[2] *Heidenhain*, Pflüg. Archiv, **90**, 115 (1902); **96**, 440 (1903); **100**, 217 (1903); see also *L. Michaelis*, *ibid.* **97**, 606 (1903); *A. Fischer*, "Fixierung, Färbung und Bau des Protoplasmas," Jena, 1899; *Pappenheim*, "Grundriss der Farbchemie zum Gebrauch bei mikroskopischen Arbeiten," Berlin, 1901. [Books in English containing some description of staining and fixing technique are: *Hogg*, "The Microscope," London, 1911; *Cross* and *Cole*, "Modern Microscopy," London, 1912. See also *Bayliss*, "Principles of General Physiology," London, 1915.—(*Trans.*)]

[3] *Fühner*, Arch. f. exp. Pathol. u. Pharmakol. **59**, 161 (1908).

[4] *A. Fischer*, p. 90 of monograph, *loc. cit.* under [2].

[5] *Freundlich* and *Poser*, Kolloidchem. Beihefte **6**, 297 (1914).

green depends, according to Fühner,[1] upon the fact that its base, in contrast to the other dyes, is a quaternary ammonium base. It is true that according to the chemical formula this is also the case for dyes such as auramine, malachite green, and methyl violet; but with these, according to Hantzsch and G. Osswald,[2] an atomic rearrangement into a pseudobase readily occurs, which according to the formula is not possible with methyl green. Perhaps the following circumstance also plays a part. The base of methyl green, as a quaternary ammonium base, is strong, hence in the solution of its salts the hydrolysis is extremely small. Now with the salts of many bases it is essentially a matter of the adsorption of the base itself, thus for instance with quinine, which is very little adsorbed by many adsorbents, in acid solutions, but is adsorbed in somewhat alkaline solution.[3] According to this we should expect that methyl green is so much less adsorbed because in neutral solution much less free base is contained than with other dyes, the bases of which are weaker. In agreement with this would be the fact that the adsorption of the methyl green is increased by addition of borax.[4] It would be of value to investigate the adsorption of this dye at constant $H^{\cdot}$-ion concentration, making use of buffer mixtures.[5]

It has as yet scarcely been tested to what extent certain dyeing properties of dyes are again met with in the case of quite different adsorbents. According to the experiments with bole, fibrous alumina and charcoal just mentioned, chrysoidine would be, in contrast to methyl green, a particularly strongly adsorbed dye. To what extent it is distinguished in this direction in microscopical staining should be examined. Some other dyes are said to have special peculiarities[6]: Victoria blue to dye especially elastic fibres, induline sulphonic acid to stain the anthrax bacillus, otherwise only stainable with acid dyes, Bordeaux BX not to stain the otherwise acidophilic centrosomes. Now they are all colloidal, and this behaviour may perhaps be explained by their being taken up, not by exchange adsorption, but by the adsorption of the whole molecules; hence it may be due, as in the dyeing of cotton with substantive dyes, to a special adsorption affinity.

Phenomena of displacement also become distinctly evident in these microscopic staining methods, for instance when it is necessary to wash out the fixation medium with which the cells have first been treated, before it is possible to stain them successfully. Only one example may be mentioned; tannin is frequently employed for fixation. If it is not removed by washing out it hinders staining both with basic and with acid dyes. The explanation for the basic dyes is that they enter into reaction with tannin (see p. 754), give coarser micellæ, and hence under the conditions of experiment do not arrive at the points to be stained. But the acid dyes show no reaction of this kind with tannin. We can only assume that they are unable to displace the strongly adsorbed tannin from the interface to be stained.

[1] Ber. d. deutsch. chem. Ges. **39**, 2437 (1906).
[2] *Ibid.* **33**, 278 (1900).
[3] *Rona* and *Bloch*, Biochem. Zeitschr. **118**, 185 (1921).
[4] *A. Fischer*, p. 93 of monograph, *loc. cit.*, p. 756.
[5] It should be noted in dyeing with methyl green that it is frequently contaminated by methyl violet, which may be removed by shaking out with amyl alcohol (*A. Fischer*, p. 756). The contamination of dyes with other dyes, also with organic foreign substances, is altogether an important source of error in these investigations; upon this depends probably the disturbance described by *Drooglever Fortuyn* [Zeitschr. f. physik. Chemie, **90**, 236 (1915)] in the adsorption of fuchsine on charcoal [cf. *Kruyt* and Frl. *van der Made*, Koninkl. Akad. v. Wetensch. Amsterdam, **26**, 252 (1917)].
[6] See *Pappenheim*, pp. 109, 112, 211 of monograph *loc. cit.* p. 756.

The similarity which shows itself here between the taking up of tannin as fixative and that of dyes, is not merely superficial. Concerning *tanning*,[1] particularly tanning by vegetable and organic tanning agents, but not by formaldehyde, the same may be said fundamentally as concerning dyeing. The hide is a gel, just as are fibres, and further, it is an amorphous gel. The solutions of vegetable tanning agents, which alone we will consider here in further detail, are probably all semicolloidal. This is not to be doubted as regards *tannin*, which is well known to be a compound of glucose and gallic acid. According to Navassart [2] it has no definite solubility in aqueous solution. Concentrated solutions are jelly-like, and under the ultramicroscope a Tyndall cone is to be seen. It dialyses in course of time completely through membranes such as parchment and fish-bladder. Whether the part dialysing first has the same composition as the original tannin, is controversial. Navassart holds it to be highly disperse tannin, Haller [3] remarks that it differs from it in various colour and precipitation reactions. It is doubtless not tannic acid, which however is always formed to a certain extent by hydrolysis in aqueous tannin solutions.[4] The taking up of tannin by hide powder in aqueous solution corresponds in the first stage (in point of time) entirely to a reversible adsorption obeying the ordinary isothermal.[5] The same is true for its adsorption by fibrous alumina.[6] The adsorption mixture of hide powder and tannin has however at first not the properties of leather. It only acquires them in course of time,[7] that is, it becomes brown, does not give up tannin upon washing with water, and becomes resistant to the attack of water or dilute alkali. This alteration appears very plainly from the following behaviour. Alcohol removes the tannin very readily from the hide powder, since it is only weakly adsorbed by the latter from alcoholic solution. If shortly after the formation of the adsorption mixture the tannin is washed out with alcohol, the washed hide powder, when brought into aqueous tannin solution, takes up tannin again freely; the more the colloidal mixture is aged, the less tannin is the hide powder obtained by washing with alcohol able to take up.

In flocculating gelatine sols with tannin we are dealing with an adsorption of the tannin by the gelatine according to the laws of adsorption; gelatine gels also take up tannin in a similar manner. As in the case of adsorption by hide powder, the tannin in this case also can be washed out less and less easily as time goes on. As hide powder adsorbs tannin but little in alcoholic solution, a gelatine solution is not precipitated by alcoholic tannin solution. Animal charcoal and fibrous alumina on the other hand adsorb tannin also in alcoholic solution according to the adsorption isothermal.[8] Tannin is known to be in true solution in alcohol (see p. 559).

[1] See *Procter*, "I.B.A. Rep. on Colloid Chemistry," p. 5. Practical books are *Flemming*, "Practical Tanning," London, 1916; *Procter*, "Principles of Leather Manufacture," London, 1903.

[2] Kolloidchem. Beihefte **5**, 299 (1914).

[3] Kolloidzeitschr. **23**, 100 (1918).

[4] *Neuner* and *Stiasny*, Collegium, 1910, p. 137.

[5] *Stiasny*, Collegium, 1908, p. 118; Kolloidzeitschr. **2**, 257 (1908); *R. O. Herzog* and *Adler*, *ibid.* **2**, II Suppl., p. iii (1908); *J. v. Schroeder*, Kolloidchem. Beihefte **1**, 1 (1909).

[6] *H. Wislicenus*, Kolloidzeitschr. **2**, II Suppl., p. xi (1908).

[7] The following experiments were carried out by *J. v. Schroeder* (*loc. cit.*).

[8] These data rely on measurements by *J. v. Schroeder*, *loc. cit.* under [5]. Concerning the microscopic appearance of tanned gelatine and the stratifications appearing therein, see *Moeller*, Kolloidzeitschr. **19**, 205 (1916); **20**, 257 (1917).

There is a considerable number of biological processes which distinctly resemble those just discussed, in so far as a dissolved substance, in true or colloidal solution, is at first adsorbed by a gel-like adsorbent; this first process, which naturally also regulates the amount of substance acting in the gel, is followed by a second, a chemical process, which forms the essential part of the biological process in question. This is true, for instance, for the action of many poisons and also of many disinfectants. Thus the dependence on the concentration of the destructive action of corrosive sublimate on living organisms may be calculated according to the adsorption isothermal [1]; the effective amount is therefore also an adsorbed amount. Substances which depress the adsorbability of $HgCl_2$ upon charcoal, such for instance as NaCl and HCl—they cause the formation of less adsorbable complex ions, such as $HgCl_3'$ and $HgCl_4''$—diminish its disinfecting power.[2] With sublimate an adsorption on cells and biologically important interfaces has been proved, for instance on blood corpuscles [3] and yeast.[3] R. O. Herzog and Betzel [4] have also shown for some other disinfectants, such as phenol and chloroform, that they are taken up by yeast according to the adsorption isothermal. The same is true of the adsorption of many alkaloids, such as that of veratrin, by the heart-muscle of a maritime snail *Aplysia limacina*.[5] The experiments of Herm. Wieland [6] are also worthy of note. Frogs' hearts poisoned by Na desoxycholate may be restored by allowing this substance to be displaced from the interface at which it is adsorbed by capillary-active substances such as Na oleate, camphor, xylene, or also by removing it by aid of a second adsorbent, such as charcoal. Further examples of such adsorptions will be discussed in connexion with enzyme processes (see p. 767).

The Kinetics of Reactions accelerated by Enzymes and of other Reactions taking place under Biological Conditions [7]

By enzymes or ferments we understand certain substances—no doubt compounds of high molecular weight or mixtures of substances—which occur in the organic world and are able to accelerate in a pronounced manner a number of chemical reactions. The chemical nature of enzymes has not yet been definitely elucidated; the difficulties to be overcome lie mainly in the fact that they occur in nature in extremely small amount, and either are themselves very readily decomposed and of high molecular weight, or occur as very unstable organic compounds combined with substances of high molecular weight as carriers.

Colloido-chemical influences are important in very many ways in connexion with enzymes. Leaving aside for the present the question as to

[1] *H. Morawitz*, Kolloidchem. Beihefte **1**, 301 (1910). Concerning the relation between the adsorbability of a substance and its disinfecting power see *Bechhold* [Zeitschr. f. Hygiene u. Infektionskrankheiten, **64**, 113 (1909); Kolloidzeitschr. **5**, 22 (1909)].

[2] *L. Michaelis* and *Rona*, Biochem. Zeitschr. **97**, 94 (1919).

[3] *H. Morawitz*, Kolloidzeitschr. **6**, 259 (1910).

[4] Zeitschr. f. physiol. Chemie, **67**, 309 (1910); **74**, 221 (1911). Concerning the adsorption of dyes by yeast see *Rohland* and *Heyder* [Kolloidzeitschr. **17**, 139 (1915)].

[5] *Straub*, Arch. d. fisiol. **1**, 65–66 (1904).

[6] Arch. f. Exp. Pathol. u. Pharmakol. **86**, 92 (1920); **89**, 47 (1921).

[7] See in this connexion *Effront*, "Biochemical Catalysts," Trans. Prescott, New York, 1917; *Bayliss*, "Nature of Enzyme Action" (Longman's monographs on Biochemistry), London, 1908; *Euler*, "General Chemistry of the Enzymes," trans. Pope, London, 1912.—(*Trans.*)

whether they are simple substances or not, it may be said in the first place that their solutions are doubtless always colloidal or semicolloidal. From Table 143, p. 547, according to R. O. Herzog's experiments it appears that enzymes such as pepsin and rennet have diffusion coefficients of the same size as the proteins.[1] Enzymes may further be characterized by their isoelectric point,[2] a fact that suggests their protein-like nature.

Like most semicolloids they are decidedly adsorbed by adsorbents such as charcoal, bole, etc.,[3] and a similar behaviour occurs as with dyes, that is to say, the charge of the adsorbent is of influence as regards the adsorption of a more basic or more acidic colloidal ion. Thus Hedin[4] found that two proteolytic enzymes present in the spleen are both strongly adsorbed by charcoal in neutral solution; kieselguhr, however, only adsorbs the one which has a strong catalytic action in alkaline solution, and not the other, which acts in acid solution. Since the negative kieselguhr will tend to adsorb colloidal kations, and not colloidal anions (cf. p. 209), we must conclude that the enzyme active in alkaline solution forms colloidal kations by preference in neutral solution, and the other enzyme colloidal anions. L. Michaelis[5] found a number of further examples. Invertase, always negative, is adsorbed by positive alumina, not by negative kaolin. The $H^{\cdot}$ and OH' ion content of the solution is of decisive influence with many amphoteric enzymes. In acid solution, in which chiefly colloidal kations are formed, many enzymes are only taken up by negative adsorbents such as kaolin; in alkaline solution, colloidal anions being formed, only by positive adsorbents such as alumina. The adsorption isothermal frequently holds, but the adsorption is not reversible, doubtless because coagulation, and chemical changes corresponding to denaturing, occur in the adsorption layer, as indeed is well known in the case of proteins (see p. 537). The solutions of ferments are inactivated by shaking.[6] This unquestionably depends upon the phenomenon described above in connexion with the proteins (cf. p. 535) that a protein may be removed from the solution by shaking.[7] With the ferment solutions, therefore, the enzyme will be correspondingly adsorbed at the air surface, but then suffers changes through coagulation and denaturing which prevent it passing into solution again.

It is, as we have said, still an open question whether the enzymes are single chemical compounds, or whether the substance really responsible for the acceleration of the reaction is some very reactive compound of low molecular weight which is adsorbed on a protein-like substance. The diffusion constant and the isoelectric point would in the latter case be

[1] Re the diffusion constant of invertin, see also *v. Euler* and *Kullberg*, Zeitschr. f. physiol. Chemie, **73**, 340 (1911); *v. Euler, Hedelius,* and *Svanberg, ibid.* **110**, 190 (1920).

[2] *L. Michaelis* and *H. Davidsohn*, Biochem. Zeitschr. **28**, 1 (1910); **30**, 481 (1911); *L. Michaelis, ibid.* **33**, 182 (1911); *L. Michaelis* and *Rona, ibid.* **57**, 70 (1913); **58**, 148 (1913); *Sörensen*, Ergebn. d. Physiol. **12**, 393 (1912).

[3] A comprehensive description in *Hedin's* "Grundzüge der physikalischen Chemie in ihrer Beziehung zur Biologie," p. 131 *et seq.*, Wiesbaden, 1915. Concerning the application of adsorption to the preparation of pure invertin, see *Willstätter* and *Rache*, Lieb. Ann. **425**, 1 (1921).

[4] Biochem. Zeitschr. **2**, 112 (1906).

[5] Biochem. Z. **7**, 488 (1907); **10**, 283 (1908); **12**, 26 (1908).

[6] *Abderhalden* and *Guggenheim*, Zeitschr. f. physiol. Chemie, **54**, 331 (1907); see also *S.* and *S. Schmidt-Nielsen, ibid.* **60**, 426 (1909); **68**, 317 (1910); *Shaklee* and *Meltzer*, Physiol. Zentralbl. **23**, 3 (1909).

[7] See *R. O. Herzog* in *Oppenheimer's* "Die Fermente und ihre Wirkungen," 4th Ed., Leipzig, 1913, p. 882 *et seq.*

properties of the carrier, and not of the enzyme itself. One might regard it as a contradiction to such a view that the diffusion of the enzyme in the experiments referred to above (p. 760) obeys the usual laws of diffusion and a well-defined diffusion constant can be determined. The enzyme content is determined during diffusion by the reactions caused by the enzyme, and therefore it is the diffusion of the ferment molecules that is followed, and not that of the carriers. If during diffusion a certain separation of carrier and true enzyme should take place, it would be difficult to understand why the course of the diffusion is so regular and slow. But a separation of this kind need not necessarily occur, if the number of enzyme molecules is very small and they are freely adsorbed by the carrier-molecules.

Much is in favour of the view that certain enzymes, such as the catalases, are characterized by a content of heavy metal molecules, such as Fe and Mn, which readily pass from one stage of oxidation to another, and hence are in other respects prominent as catalysts.[1] In this connexion the reader may be reminded (cf. p. 225) how often and strongly such metals, when adsorbed at suitable interfaces, may accelerate processes.

In the cell very different kinds of enzyme reactions take place without disturbing one another. This compels us to take the view that the enzymes are more or less locally bound in the cell, so that the reactions can take place at different points.[2] One will therefore suppose that the ferments are attached to different particles of the protoplasm or to different points of the plasma membranes. The attachment may be so loose that the ferments can even diffuse out of living cells ; in other cases it is released when the cells die. Finally, enzymes are known which it has not been possible to separate by any means from the rest of the cell.

Enzyme reactions do not therefore take place entirely in colloidal solutions, but frequently in gels to the micellæ of which enzymes are bound. Hence they cannot be considered exclusively in connexion with sols, but require that gels also shall be taken into account. At times there has been a tendency to refer all peculiarities of enzyme reactions to their taking place at interfaces. This is probably not correct ; at least it is difficult to explain why stereochemical influences are important in enzyme processes Thus, for example, E. Fischer[3] found that *α-d*-glucoside is attacked by invertase and maltase, *α-l*-glucoside not. The specificity is frequently not so strict that only the dextro-form, say, of a stereoisomeric compound reacts under the influence of the ferment, while the lævo-form does not ; but the former may do so much more rapidly. If we wish to refer this fact to known ones, we shall think of purely chemical actions and reaction velocities, since a specific adsorption is not yet known (though we may regard it as possible, cf. p. 538), let alone one so specific as to depend upon the stereoisomeric structure of adsorbent and adsorbed substance. On the other hand, there is perhaps hardly a single ferment reaction, the time-course and mechanism of whose action can be understood without taking capillary chemical influences into account. In the following only a few examples will be given in which they appear particularly plainly.

Certain enzymes, the so-called *catalases*, able to decompose hydrogen peroxide, are very widely distributed in nature. The time-course of the

[1] See e.g. *Willstätter* and *Stoll*, Lieb. Ann. **416**, 21 (1918).

[2] *Hofmeister*, "Die chemische Organisation der Zelle," Naturwissenschaftl. Rundschau, 1901, p. 581 ; see also *Ruhland*, Biolog. Zentralblatt. **33**, 337 (1913).

[3] Ber. d. deutsch. chem. Ges. **27**, 2985 (1894).

H_2O_2 decomposition produced by them may be largely referred, as Waentig and Stecher [1] have shown, to adsorption processes. There exists a certain similarity to the decomposition caused by metallic sols, along with pronounced differences. The investigators in question deal particularly with *hæmase*, the catalase of blood, and then catalases which may be obtained from the body fluids of caterpillars and pupæ. Hæmase was thoroughly investigated by Senter.[2] The reaction equation of the first order assumed by him to hold throughout, and his view of the reaction as a simple Nernst-Brunner diffusion process, have been shown by Waentig and Steche not to be correct. In many cases the constants calculated according to a unimolecular reaction increase greatly in course of the reaction, in others they decrease. One will always be inclined to refer an increase in the unimolecular constants to an adsorption of the substrate,[3] as was also done in the case of the catalytic decomposition of H_2O_2 by Pt sols (see p. 490). For an equation

$$-\frac{dc}{dt} = kc^{\frac{1}{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

with a fractional exponent reproduces an increase of this kind well, and such an equation states that the reaction velocity depends upon the amount of the adsorbed substance. As remarked earlier (p. 491), this equation is not without ambiguity. It may on the one hand be the expression of a chemical reaction, in which only the amount of the substance adsorbed enters into reaction. But it may also reproduce a diffusion process, if the gradient of concentration into a deeper-lying layer does not depend upon the concentration of the solution, but upon the concentration of the substance in the adsorption layer. In the case of Pt catalysis of H_2O_2, the interpretation on the basis of a chemical reaction was preferred, especially as the temperature coefficient was so much larger than with macro-heterogeneous catalysis. With the catalases we are forced to the view of a diffusion reaction, since the temperature coefficient is small, usually below 1·3 for 10° increase (between 0° and 20°). Besides, in the case of the less rigid, more hydrophilic micellæ of the catalase, one can more easily imagine a diffusion gradient within the adsorption layer, than with the rigid micellæ of a Pt sol.

That a decrease is also observed in the unimolecular constants is explained by Waentig and Steche as follows: The oxygen formed during the reaction is likewise adsorbed by the catalase, displaces H_2O_2 from the adsorption layer, and thus causes a retardation of the reaction. It is evident that the two influences may cancel one another and cause the reaction to take a unimolecular course. The following experiment tells strongly in favour of this view. If the oxygen is removed as quickly and thoroughly as possible by shaking the reaction mixture in a vacuum while the reaction is taking place, the inhibition due to the O_2 can be eliminated; the unimolecular constants, which fall in the case of the unshaken mixture, increase with that shaken *in vacuo*. Conversely, the reaction is considerably inhibited from the first if before it commences oxygen be passed for some time through

[1] Zeitschr. f. physiol. Chemie, **72**, 226 (1911); **76**, 177 (1912); **79**, 446 (1912); **83**, 315 (1913).

[2] Zeitschr. f. physik. Chemie, **44**, 257 (1903); **51**, 673 (1905); further also Zeitschr. f. physiol. Chemie, **74**, 101 (1911).

[3] The substance which reacts under the influence of the enzyme is described as the substrate.

the ferment solution. Here we are not dealing with a weakening of the ferment as a result of oxidation ; for if during the course of such a reaction inhibited by pre-treatment with O_2 the O_2 was removed by shaking *in vacuo*, the constants increased and finally attained values such as would have appeared with the reaction without pre-treatment by O_2.

All other observations also agree with this view. At higher H_2O_2 concentrations the constants fall less, since the inhibition due to O_2 is small ; at low H_2O_2 concentrations the initial constants are higher than with larger ones, since in accordance with the adsorption isothermal relatively more is adsorbed at low concentrations. An inhibitory influence is also produced by the adsorption of other gases, even of nitrogen. The velocity is practically proportional to the enzyme concentration (perhaps a slight decrease at large concentrations). This is to be expected if it depends on the adsorption of the H_2O_2, and the amount adsorbed is small compared with the total amount in solution. We do not therefore meet with an increase in velocity greater than proportional to the rise of ferment concentration, as in the case of metal sols (cf. p. 494). Perhaps with the small enzyme micellæ and their correspondingly larger specific boundary surface the conditions for a rapid attainment of adsorption equilibrium are more favourable.

As with the metal sols we meet also in the case of catalases with the action of poisons, substances which depress the reaction velocity often when present in very low concentration. Here the whole nature of the effect, reversibility, dependence upon concentration, and so on, favours an adsorption ; with the limitations already discussed in connexion with metallic sols. The influence of acids and alkalis is unmistakably other than in the case of metal sols. A maximum of catalytic action lies, with many catalases, at an OH′-ion concentration somewhat higher than that of pure water ; at higher H· and OH′ ion contents the velocity of decomposition decreases considerably with most catalases. But it attains the original value again when by neutralization the H·-ion concentration is restored to that of pure water. We shall be less disposed to consider a coagulation at the large H· and OH′ ion concentrations, and a peptization at the small OH′-ion concentration, although they may have a subsidiary influence. We shall rather assume with Waentig and Steche that we are dealing with the hydrophilic sol of an amphoteric substance—perhaps of a protein or metal protein compound. H· and OH′ ions lower in a manner well known (see p. 570) the concentration of the neutral micellæ, produce colloidal ions, and a maximum of catalysis with a maximum adsorption of H_2O_2 might go with a maximum content of neutral micellæ.

The similarity between the action of metallic sols and enzyme solutions is also expressed in reactions of another kind. Thus according to Bredig and Sommer [1] Pt and Ir sols—Pd and Au sols much less—accelerate the reaction upon which the Schardinger milk ferment acts : the reduction of formaldehyde by methylene blue.

A variation similar to that in the case of the catalases was found by Abderhalden and Fodor [2] in the decomposition of polypeptides under the influence of a ferment contained in yeast extract. The reaction is of the first order in neutral solution (they always worked in buffer mixtures at constant H·-ion concentration), in acid solution the unimolecular constants rise, in alkaline they fall. But in acid solution the course could be satis-

[1] Zeitschr. f. physik. Chemie, **70**, 34 (1910).
[2] Fermentforschung, **1**, 533 (1916) ; **2**, 74 (1917).

factorily represented by equation (1); we are therefore dealing with an adsorption of the peptide on the ferment. The appearance of a unimolecular reaction in neutral solution is interpreted by the investigators above named on the basis that the adsorption exponent can assume the value unity—this was frequently observed for the adsorption of peptides by charcoal in dilute solutions—and equation (1) then becomes a reaction equation of the first order. The decrease in the unimolecular constants in alkaline solution is explained on the grounds of an ageing of the enzyme. The great dependence upon the H˙ and OH′ ion concentration is probably due to the formation of colloidal ions and leads us to expect a considerable influence of hydration. With this agrees a curious and complicated change in the course of the reaction effected by neutral salts [1]; the lyotropic series is recognizable therein, but confused by the fact that apparently several equilibria are displaced by the salts. Since with enzymes swelling, and in general hydration equilibria, are important, it is intelligible that ionic antagonism also appears in ferment reactions.[2]

A further example in which the influence of adsorption is clearly felt is the reaction, investigated by Bodenstein and Dietz,[3] of a fat-hydrolysing enzyme, a lipase, contained in the pancreas. This is not found in colloidal solution, but firmly adherent to finely triturated pancreas, which, as a swelling powder, is uniformly distributed in the liquid by energetic stirring. They followed the formation and decomposition of amyl butyrate (into *n*-butyric acid and *i*-amyl alcohol) in amyl-alcoholic solution. With constant concentrations of alcohol and water an equilibrium is set up, which may be represented by an equation

$$\frac{(\text{ester})^{\frac{1}{2}}}{(\text{acid})} = \text{K} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here again the brackets indicate concentrations. The half-power of the ester concentration is obviously to be explained by the equilibrium being set up in an adsorption layer, and the ester distributing itself between solution and pancreas powder according to an adsorption isothermal.

It is curious that the equilibrium set up under the influence of the enzyme lies at an ester content of about 75 per cent.; in homogeneous solution, on the other hand, under the catalytic influence of the H˙ ion at about 85 per cent. This is not a matter of false equilibria; on the contrary, also with the enzymes the equilibria are set up readily from either side. This behaviour is not necessarily in contradiction with the Second Law of Thermodynamics, for the ferment equilibrium certainly differs from homogeneous equilibrium in that interfacial forces are of influence. Apart from the adsorption of the ester this fact appears in the sensible swelling of the pancreas powder. Hence the distribution of water between liquid and ferment carrier is also influenced by capillary-chemical effects. These surface influences may very well suffice to produce such a displacement of the equilibrium in the liquid, for, as appears from its position, the work required to displace the equilibrium is small.[4]

The velocity of ester formation and ester decomposition corresponds to

[1] *Abderhalden* and *Fodor*, Fermentforschung, **4**, 191 (1920).

[2] *Neuschloss*, Pflüg. Arch. **181**, 45 (1920).

[3] Zeitschr. f. Elektrochemie, **12**, 605 (1906); further *Dietz*, Zeitschr. f. physiol. Chemie, **52**, 279 (1907).

[4] See on this point also *Haber's* note to *R. O. Herzog* in *Oppenheimer's* "Die Fermente," pp. 937–8.

that to be foreseen from the equilibrium equation (2). Thus ester formation may be well represented by an equation

$$\frac{d(\text{ester})}{dt} = k_1(\text{acid}) - k_2(\text{ester})^1 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It states that the amount of ester adsorbed determines the reaction velocity ; it is therefore assumed that the adsorption equilibrium is set up quickly, compared with the velocity of the chemical reaction taking place in the adsorption space.

It will probably be possible to interpret successfully the time-course of many other enzyme reactions, the course of which has been frequently represented by very complicated equations, by aid of capillary-chemical processes. Thus, we meet with cases which are similar to those discussed for catalases, in that under certain limiting conditions an equation of the first order holds, from which, however, serious divergences appear as soon as the range of temperature, concentration, and so on, is further extended. Here we will only draw attention to the description of enzyme reactions in Hedin's book above mentioned (p. 760). He repeatedly regards the ferment as colloidally dissolved, takes into account the adsorption of the substrate on the enzyme, and if the substrate is itself colloidal, he thinks of the usually irreversible adsorption compounds between two colloids. Regarding the further time-course he prefers the view that this adsorption takes place quickly, that diffusion processes recede in importance, and that it is mainly a matter of the velocity of chemical reactions in the adsorption space. I do not think, however, that it is permissible to exclude diffusion processes without further question, especially those taking place through adsorption layers. Thus in dealing with the kinetics of the oxidation of phenylthiourea on blood-charcoal,[1] which could throughout be interpreted as a diffusion process, attention was drawn to the fact that its course may be represented by the so-called Schütz's rule, which has been found to hold with so many enzyme processes. It states that the amount decomposed is proportional to the square root of the time and of the enzyme concentration. The similarity is perhaps more than purely superficial.[2]

An important means of characterizing enzyme processes—and quite generally reactions under biological conditions—and of determining under what conditions they take place, consists in determining the dependence of the reaction velocity upon the presence of foreign substances. It is especially the substances exerting an inhibition which are of importance. We may with O. Warburg [3] separate the unspecific capillary-active substances from the specific, such as hydrocyanic acid, carbon monoxide, and so on. It has already been discussed on p. 229 how, according to Traube's rule, capillary-active substances may inhibit a series of adsorption reactions more and more strongly as we ascend the homologous series. Hence if an action of capillary-active substances of this nature is observed, the converse conclusion may be drawn that the reaction is taking place on a surface. O. Warburg, Meyerhof, and others have successfully applied this principle in various directions. Thus Meyerhof [4] was able to show that the action

[1] See *Freundlich* and *Bjerke*, Zeitschr. f. physik. Chemie, **91**, 38 (1916).
[2] Regarding another explanation of *Schütz's* rule see *Arrhenius* [Medel. f. Nobel-Inst. **1**, No. 9 (1908)].
[3] Ergebn. d. Physiol. **14**, 290 (1914).
[4] Pflüg. Archiv, **157**, 251 (1914).

of invertase is inhibited by urethanes according to Traube's rule, while in homogeneous solution, in the case of the inversion of cane-sugar by $H^{\cdot}$ ions, these substances had no effect. Hence it must be assumed that even in the case of this enzyme, which probably has not a very large molecular weight (see p. 546), the process takes place at an interface. And O. Warburg [1] has shown by this method that a number of important biological processes, such as respiration and assimilation of CO_2, take place at interfaces. The following table shows how far Traube's rule is confirmed, and how plainly the strong capillary activity of aromatic substances makes itself felt. The concentrations of inhibitory substance given are those which depress fermentation by 50 per cent., and the respiration of cells of bird's blood 30 to 70 per cent.

TABLE 188

Inhibition of Biological Processes by Capillary-active Substances.[2]

Substance.	Concentration (millimol per litre) which inhibits Fermentation in living Yeast Cells by 50 per cent.	Concentration (millimol per litre) which inhibits Respiration of living Bird Blood Cells by about 30 to 70 per cent.
Ethyl urethane	404	393
Propyl urethane	194	99
Isobutyl urethane . . .	60	43
Phenyl urethane	7·3	4·3

It further appeared that the sensitiveness of various reactions to these influences is very different. Thus the assimilation of carbon dioxide proved to be particularly sensitive to urethanes, much more sensitive than respiration; indeed, the concentrations which just produced an effect were smaller than those effective in narcosis, which were already regarded as particularly small.[3]

The inhibition of these reactions by hydrocyanic acid was also followed by O. Warburg. He assumes as the cause of this action that heavy metal atoms present at the interfaces are loosely combined as complex cyanides, and hence an accelerating effect originally exerted by them removed (see p. 232). The sensitiveness towards hydrocyanic acid is also very different for different reactions. This, as well as the above-mentioned strong sensitivity towards capillary-active substances, makes it possible to disentangle the often very complicated network of biological processes which are intermingled with one another, by completely stopping one by means of a suitable addition of an inhibitory substance, while the other still goes on.

It may be further remarked that the simultaneous inhibition of the respiration of bird's blood cells by a capillary-active substance and hydrocyanic acid takes place entirely as we should expect in the case of a displacement adsorption of two substances, whereby one substance, the capillary-active, is present in much greater concentration than the other, the hydrocyanic acid. The inhibition due to the mixture was smaller than corresponded

[1] Zeitschr. f. physiol. Chem. **69**, 452 (1910); Ergebn. d. Physiol. **14**, 253 (1914); Biochem. Zeitschr. **100**, 230 (1919); **103**, 188 (1920).

[2] *O. Warburg*, Ergebn. d. Physiol. **14**, 295 (1914).

[3] *O. Warburg*, Biochem. Zeitschr. **100**, 264 *et seq.* (1919).

to the sum, indeed, in many cases less than that due to the HCN alone, since this is displaced from the surface by the capillary-active substance, without the concentration of the latter sufficing to screen off the residual valencies of the active heavy metal atoms.[1]

The concentration function with which the capillary-active substances produce their effects has only been examined in a few cases. O. Warburg [2] found that in the case of the inhibition of CO_2 assimilation in light by phenyl urethane the inhibition, as a function of the external concentration of the phenyl urethane, follows the ordinary adsorption isothermal, as one would expect if it were a matter of a surface reaction.

In the case of enzyme reactions Rona has recently described good examples of pronounced dependence upon concentration. Thus quinine [3] inhibits the action of invertase on cane sugar entirely in accordance with an adsorption; the relative inhibition may be expressed in its dependence upon the quinine concentration by the usual isothermal; the adsorption takes place very quickly and reversibly, hence also independently of the order in which the substances taking part in the reaction are mixed; the temperature coefficient is small. The dependence upon H·-ion concentration is strong in the sense that the quinine base, possibly in a tautomeric form, is much more freely adsorbed than the quinine salts; in acid solution the inhibition is correspondingly smaller. The derivatives of quinine—optochin, eucupin, and vuzin—behave similarly; vuzin, the most active at the surface water—air, also exerts the strongest inhibition.

If we pass to the behaviour of the substances exerting a specific inhibition, we should be entirely wrong in regarding generally every inhibition by foreign substances as a typical adsorption; on the contrary, as is usual in the case of biological processes, every possible case is actually present. Thus Rona and E. Bach [4] found that the poisoning of invertase by *m*- and *p*-nitrophenol has a completely different character: the poisoning of the enzyme proceeds slowly in the manner of a slow, irreversible chemical reaction; the dependence upon the concentration is characterized by a threshold value; below a certain limiting concentration no inhibition can be observed; it first appears at a sufficiently large concentration and then increases in simple proportion to this concentration; the temperature coefficient for 10° amounts to 1·87. Everything agrees with a chemical process in the true sense—we may recall the taking-up of picric acid by diphenylamine (cf. p. 237).

That the poisoning of invertase by sublimate has the character of a completely reversible chemical process, was already shown by v. Euler and Svanberg.[5]

The differences are no less great when we pass to other enzymes, which act in a different medium. Thus it appeared that the influence of atoxyl,[6] quinine,[7] and other compounds upon a lipase contained in the blood serum of men and animals follows quite different laws from that of quinine upon invertase. The reaction followed was the hydrolysis of tributyrin. The adsorption isothermal did not hold for the inhibition by foreign substances;

[1] *O. Warburg*, Zeitschr. f. Physiol. **76**, 331 (1911); Ergebn. d. Physiol. **14**, 304 *et seq.* (1914).
[2] Biochem. Zeitschr. **103**, 196 *et seq.* (1920).
[3] *Rona* and *E. Bloch*, Biochem. Zeitschr. **118**, 185 (1921).
[4] Biochem. Zeitschr. **118**, 232 (1921).
[5] Arch. f. Kemi, Mineral. och Geol. **7**, No. 27 (1920).
[6] *Rona* and *E. Bach*, Biochem. Zeitschr. **111**, 166 (1920).
[7] *Rona* and Frl. *Reinicke*, *ibid.* **118**, 213 (1921).

instead, the constant of the reaction velocity decreased with increased poison content, and, as a matter of fact, proportionally to the logarithm of the latter. The order in which the reacting substances were mixed had a great effect on the magnitude of the inhibition; it was greater when the foreign substance reached the surface of the enzyme first. It is probable that this difference is due less to a difference between the two ferments themselves than to the environment in which the reaction takes place: in the case of invertase in comparatively pure solution, undisturbed by other colloids; in the case of lipase in serum, a solution rich in other colloids and foreign substances. The distribution of the poison between the enzyme and other colloids, or protective actions exerted by other colloids, are perhaps the reasons why the inhibitory action of foreign substances on lipase is so different from that on invertase.

Since the ferments themselves were adsorbed at interfaces, the relationships, such as they may exist for instance in the cells, become very complicated on account of the adsorption of the enzyme at interfaces such as those of the structural elements of the cells, so that fermentative processes may be greatly influenced. The number of possibilities is great; by the ferment being largely removed by adsorption from the solution, the velocity of the fermentative process may be retarded, if the substrate under these circumstances is not able to reach the adsorbed enzyme, because it is perhaps not adsorbed. On the other hand the course of the process may be accelerated if the substrate is likewise adsorbed, and enzyme and substrate react more quickly in the adsorption space. We may recall in this connexion the accelerated decomposition of H_2O_2 by the simultaneous presence of metallic salts on glass surfaces (p. 226).

Hedin [1] made experiments in this direction, thus in the action of charcoal upon the decomposition of casein by trypsin and upon the coagulation of milk by rennet. In both cases an inhibition was caused by the adsorption of the enzyme upon the charcoal. Since here the adsorption is not reversible, or only so to a limited extent (see p. 537), the order in which the reacting substances are mixed makes a great deal of difference; the inhibition is greater when charcoal and enzyme are mixed first, since the substrate subsequently added is only able to displace comparatively little enzyme, while if the charcoal and substrate are mixed first, more enzyme remains in solution. But some ferment will usually be displaced from the charcoal surface even if the substrate is added last. Just as the substrate effects this, so do other strongly adsorbable substances, such as the saponins,[2] as is readily understood. Hedin also explains the inhibition experienced by enzyme reactions in the presence of serum and proteins on the basis of a removal in this manner of the enzyme from solution.

On the other hand, in the case of the phenomena investigated by O. Warburg [3] it may be a matter of the second case. He pointed out that for many processes, such as alcoholic fermentation and the respiration of various cells, the structure of the cell is of importance. If it be destroyed, say by trituration with sand, the processes named are greatly retarded; hence it is probable that in, say, fermentation, the sugar in the cells, where the active mixture of enzymes, the zymase, is adsorbed on the cell structure,

[1] Biochem. Journ. **1**, 484 (1906); **2**, 81 (1906); Zeitschr. f. physiol. Chemie, **60**, 85 (1909); **63**, 143 (1909).

[2] *Jahnson-Blohm*, Zeitschr. f. physiol. Chemie, **82**, 178 (1912).

[3] Zeitschr. f. physiol. Chemie, **70**, 413 (1911); Pflüg. Archiv, **145**, 277 (1912); a comprehensive description in Ergebn. d. Physiol. **14**, 313 *et seq.* (1914).

is more rapidly decomposed then when it only meets the zymase in colloidal solution.

B. MIST AND SMOKE

A mist is definitely regarded as a disperse structure, the dispersion medium of which is gaseous and the disperse phase liquid. One will not draw any fundamental distinction between cases in which the particles of the disperse phase are exclusively ultramicroscopic, and others in which they are somewhat larger. They cannot be very much larger, otherwise the stability of the mist is slight.

Smoke is a mist, the particles of which are solid, either crystalline or amorphous. The difference between the behaviour of mists and smokes is so small that they are usefully considered together.

Conditions for the Formation of Mist and Smoke and their Preparation

As in the case of colloidal solutions, two methods for the preparation of mist and smoke may be distinguished, condensation methods and dispersion methods. In condensation methods we have either the condensation of a supersaturated vapour or the production of a liquid by a chemical reaction in a gas. By the first method, every substance which can be quickly and freely vaporized should be capable of forming a mist.

In order that droplets may separate from a supersaturated vapour, nuclei must be present or be formed. As regards the velocity of formation of nuclei the same conditions exist as in supersaturated solution. If the supersaturation is small, the temperature therefore but little lower than the saturation temperature, then the rate of formation of nuclei is also so small that no mist is formed of itself ; it is necessary to produce artificial nuclei in order to cause its formation. With strong supersaturation and correspondingly greater cooling of the vapour the velocity of formation of nuclei is so great that nuclei are formed of themselves and a mist results.

More is known of the nature of the substances which, when introduced into the supersaturated vapour, are able to act as nuclei, and of the conditions under which they do so, than of the actual rate of formation of nuclei. Three groups of such nuclei-formers can be named ; dust, certain chemical substances, and carriers of electricity. Before we go into them in detail, we will discuss the methods which are usefully employed in investigating mists.

The *vapour jet phenomenon*, first described by R. v. Helmholtz,[1] is handy and very sensitive, although more of a qualitative nature. Water is allowed to boil energetically in a vessel and the vapour allowed to issue as a jet through an opening of 1 to 2 mm. diameter into the space to be investigated, whereby heating of the jet by the flame must be avoided. The jet of vapour is examined against a dark background, so that as far as possible light diffracted sideways reaches the eye. At some distance from the point of exit the vapour will be sensibly supersaturated on account of the cooling, but not so strongly that any considerable formation of mist takes place of itself. Under ordinary experimental conditions with the air of a room the jet appears faintly grey, only dimly contrasted with the background. If mist nuclei are introduced at the point at which it is sensitive

[1] Wied. Ann. **32**, 1 (1887); *R. v. Helmholtz* and *Richarz*, ibid. **40**, 161 (1890).

on account of supersaturation, its appearance changes completely; it becomes either a dense grey white or shows a variety of colours. This difference in appearance depends upon the various sizes and uniformity of the droplets, into which we shall go later (p. 771). The following mist nuclei which may be recognized in this manner may be mentioned: fine dust, concentrated sulphuric, hydrochloric and nitric acids, when heated and especially when they react with ammonia, ozone in course of formation or decomposition, air which has been led over oxidizing phosphorus or freshly cut surfaces of sodium or potassium, chlorine which has been illuminated by ultra-violet light; quite generally air containing carriers of electricity, hence flame gases, or air through which sparks have been passed, or which has been subjected to α, β, or γ rays, and so on.[1]

Numerical results and sharper differences between the behaviour of various nuclei are obtained when in place of the indefinite supersaturation of the jet of vapour we work with a definite supersaturation variable at will, as first done by C. T. R. Wilson.[2] He allowed a space of known volume saturated with water vapour to expand rapidly and adiabatically to a larger and also measurable volume. Since the initial temperature T_1 was known, the temperature T_2 after adiabatic expansion can be calculated from the formula

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is equal to $\frac{c_p}{c_v}$, the ratio of the specific heats. From this the vapour pressure ϱ_2, existing *after* the supersaturation has been removed, can be calculated. The vapour density ϱ' *before* the supersaturation is removed only differs from that ϱ_1 existing at temperature T_1 through the volume having been changed:

$$\frac{\varrho'}{\varrho_1} = \frac{v_1}{v_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If the ratio $\frac{\varrho'}{\varrho_2}$ is called the supersaturation S and it be borne in mind that, if the gas laws hold,

$$\frac{\varrho_1}{\varrho_2} = \frac{p_1 T_2}{p_2 T_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

then we get from (1), (2) and (3)

$$S = \frac{\varrho'}{\varrho_2} = \frac{\varrho_1}{\varrho_2}\frac{v_1}{v_2} = \frac{p_1 T_2 v_1}{p_2 T_1 v_2} = \frac{p_1}{p_2}\left(\frac{v_1}{v_2}\right)^k \quad . \quad . \quad . \quad . \quad . \quad (4)$$

p_1 and p_2 are the vapour pressures of water at the temperatures T_1 and T_2.

If ordinary air not specially freed from dust is used for such experiments a very small supersaturation at first suffices to produce mist; the dust particles act as nuclei. If this slight reduction in pressure is frequently repeated, and the mist formed allowed to settle each time, we very soon

[1] Regarding details of this section the reader may be referred particularly to *Przibram's* paper [Jahrb. d. Radioaktivität, **8**, 285 (1911); further to *Townsend* in *Marx's* "Handbuch der Radiologie," Leipzig, 1920, p. 193 *et seq.* Also *Thomson*, "Conduction of Electricity through Gases," 2nd Ed., p. 53.

[2] Phil. Trans. **189**, A, 265 (1897); **192**, 403 (1899); **193**, 289 (1899).

fail to produce mist by means of so small an expansion ; the air has been freed from dust. A much more considerable change in volume must be produced, a ratio of the volumes such as 1·25 to 1, and a supersaturation of about 4·2 (with an initial temperature of 15° to 28°) in order that mist may again be obtained. We then get comparatively few, but larger, drops—C. T. R. Wilson estimates about 100 to the cubic centimetre—which settle like a shower of rain in a few seconds ; the number of nuclei is therefore small. This behaviour is the same if the experiment is repeated after the drops have settled. We are therefore dealing with nuclei doubtless formed in accordance with the true velocity of formation of nuclei. Up to a volume ratio of 1·37 to 1, a supersaturation of about 8, the phenomenon does not sensibly alter. If the supersaturations are still larger, the picture alters strikingly and rapidly. A strong mist is formed, which takes a minute or more to settle. It shows, especially by transmitted light, distinct colours, which change, as the supersaturation increases, from deep green through reddish to greenish white, as Table 189 shows.

TABLE 189

Colours of Mist at Higher Supersaturations

Volume Ratio $\frac{v_2}{v_1}$	Colour.
1·408	Shining green.
1·412	,,
1·414	,,
1·419	Blue green } region of the sensitive
1·422	Purple } colour change.
1·424	Bright red }
1·426	Red.
1·429	,,
1·434	Reddish.
1·437	Reddish white.
1·453	Greenish white.
1·458	,,

Above a volume ratio of 1·37 the number of nuclei therefore becomes very much greater and continues to increase as far as the experiments go. At the volume ratio of " sensitive colours " of 1·42, Wilson calculates about 10^8 droplets per c.c.

The phenomena are not sensibly different when instead of air, oxygen, nitrogen, carbon dioxide, or chlorine are used, except that with chlorine, for instance, the validity of the gas laws must not be assumed and the supersaturation cannot be calculated so simply. The number of particles also appears to be greater in the case of chlorine in the region of the formation of large drops. Hydrogen behaves remarkably differently. Here also we have the condensation into fine drops above a volume ratio of 1·37, but between 1·25 and 1·37 the condensation into large drops is practically absent. The drops formed above 1·30 are so scattered that one is inclined to think of chance impurities. It would accordingly seem that the rate of formation of nuclei only takes on considerable values above 1·37. Hence doubtless the molecules of the gas play an essential part in the condensation at smaller

supersaturations, perhaps by giving nuclei, in themselves possessing too short a life, greater stability by being adsorbed on them. Hydrogen is so weakly adsorbed that it is not able to do so. If this is correct, helium should surpass hydrogen in this connexion. Whether at still greater supersaturations and lower temperatures the rate of formation of nuclei again decreases, as in the formation of solid nuclei in liquids (p. 319), is still an open question.

The degree of supersaturation is also important when the nuclei are introduced from outside. Fine dust and the active chemical substances mentioned above cause a condensation even at small supersaturations. The influence of dust is intelligible from the following considerations. That a certain supersaturation is necessary for condensation to take place does not depend simply upon too small a rate of formation of nuclei, but—as already stated upon p. 44—upon the fact that the very small drops first formed have too large a vapour pressure on account of their strongly convex surface and are not stable at all at a slight degree of supersaturation. On the dust particles, on the other hand, we have, assuming them to be wettable, surfaces of much smaller convexity, indeed even concave ; upon these surfaces of low vapour pressure the liquid can separate from the supersaturated vapour. The reader may be reminded that on a wettable surface the dew-point lies at a higher temperature than the saturation-point (cf. p. 164).

The active chemical substances are those which form solutions of very low vapour pressure with water. Hence they soon form with the molecules of the vapour comparatively large drops of low vapour pressure, upon which the vapour can easily deposit further at slight supersaturation.

The behaviour of the nuclei consisting of carriers of electricity, which can be produced by X-rays, by the rays from radio-active substances, and so forth, is essentially different. A small supersaturation does not suffice to render them effective. Only at a supersaturation of about 4 to 8, and a volume ratio of 1·25 to 1·37, do they become so ; the mist produced has quite the large-drop character otherwise usual in this region of supersaturation, except that, corresponding with the ionization, the number of drops is much greater.

The influence of carriers of electricity can be explained to a large extent when with J. J. Thomson [1] we extend the theory of the vapour pressure of small drops to the case when the drops carry free electric charges. It is qualitatively evident that the electric charge must act against the surface tension ; the charge strives to separate the molecules of the droplet, to enlarge the surface, and to lower the vapour pressure, while the surface tension exerts the opposite influence. Quantitatively we have instead of the formula on p. 45.

$$\log \frac{p_\omega}{p} = \frac{2\sigma M}{RT\varrho r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

an equation

$$\log \frac{p_\omega}{p} = \frac{M}{RT\varrho}\left\{\frac{2\sigma}{r} - \frac{e^2}{8\pi r^4}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

in which e is the charge on the droplet. Equation (5) is plotted in curve

[1] "Conduction of Electricity through Gases," 1903, pp. 149 *et seq.*

1 of Fig. 147, and equation (6) in curve 2, for the case in which the droplet carries *one* electron; the abscissæ are the radii r, the ordinates the ratios $\frac{p_\omega}{p}$. At a value r_1 for which the equation

$$r_1 = \sqrt[3]{\frac{e^2}{16\pi\sigma}}$$

holds, the vapour pressure of the charged drop is equal to that of the plane liquid surface p. But such drops cannot be formed, since there the p, r curve rises; as the droplets become larger the vapour pressure increases, and evaporation is favoured. A regular increase in size is only possible [1] when the vapour pressure decreases as the size of the drop increases, when therefore r_m, the maximum value of r, is passed; for this we have

$$r_m = \sqrt[3]{\frac{e^2}{4\pi\sigma}}.$$

The vapour pressure corresponding to r_m amounts to 4·2 times that over a plane surface when $e = 4{\cdot}8 \times 10^{-10}$. It therefore corresponds to a 4·2-fold supersaturation, which agrees well with Wilson's results.

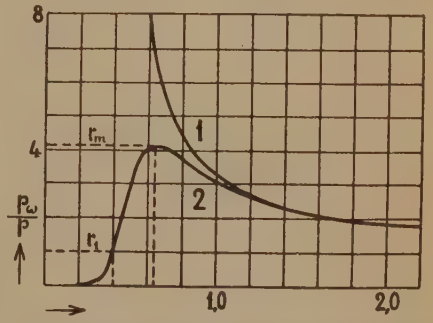


Fig. 147.—Dependence of Vapour Pressure of Small Drops upon their Size and Electric Charge.

The agreement does not remain so good when the behaviour of organic liquids is investigated in the same direction; and it further remains to be explained why also in the case of water vapour positive and negative gas ions differ.[2] The supersaturation of 4·2 relates to negative gas ions; positive ones require about a sixfold supersaturation. Hence specific influences and the nature of the carriers of electricity must still be taken into account, perhaps all the more, the more the carriers produced under various conditions are examined. Thus it is also known from the work of Lenard and Ramsauer [3] among others that ultra-violet light under certain circumstances produces nuclei in gases, which act like dust or chemical nuclei even at small supersaturations. A prerequisite is the presence of certain traces of vapours—which may be removed by liquid air—such as water and ammonia. Probably nuclei are formed under the influence of ultra-violet light consisting of chemically active substances such as hydrogen peroxide and nitric oxide. The nature of the gas is again of importance, in so far as in hydrogen these effects are very slight. Large nuclei are formed according to Owen and Hughes,[4] when a gas is cooled below a certain constant low temperature. Upon warming a gas thus previously cooled to the temperature of experiment, the condensation may disappear even at low degrees of supersaturation.

It must also be borne in mind that the Thomson theory of the action of

[1] Re the rate of further growth of droplets in a supersaturated vapour, see *Mache*, Ber. d. Wien. Akad. d. Wiss. **109**, IIa, 793 (1900).

[2] *Przibram*, Jahrb. d. Radioakt., p. 295 *et seq.* (1911).

[3] Sitzungsber. d. Heidelb. Akad. d. Wiss., 1910, 32 Abh.; 1911, 16 and 24 Abh.

[4] Phil. Mag. (6), **14**, 528 (1907); **15**, 746 (1908).

the electric carriers is defective in so far as it is not permissible with these excessively small drop sizes—r_m for instance in the case above is only $0{\cdot}63\mu\mu$—to ascribe the usual value to the surface tension. It is necessarily smaller (see p. 46); but it is still very difficult to take into account numerically this change in σ with r.

So much concerning the theory of the production of mist. A useful arrangement due to Regener [1] for the production of mist from volatile liquids (see Fig. 148) may be mentioned. A heated current of air passes through the tube A and around the vessel B containing the liquid; it then reaches the surface of the liquid and takes the vapour with it through the tube C, in which a number of electric sparks produce the condensation of the supersaturated vapour. From here the mist is passed for further investigation into a larger storage vessel.

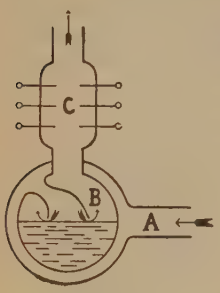


Fig. 148.

Mist or smoke is produced in many chemical reactions, when the reaction products of these gas reactions consist of difficultly volatile liquids or solids. The formation of mist in sulphuric acid manufacture is well known, also the formation of smoke in many combustion processes. Tyndall [2] observed beautiful and uniform mist in certain photochemical gas reactions, thus on illuminating mixtures of butyl nitrate and hydrochloric acid, etc.; Radel [3] upon illuminating moist chlorine.

Dispersion methods are also very suitable for the production of mists.[4] The liquid is converted into mist by means of an atomizer. In this way, not merely comparatively mobile liquids, but also viscous liquids or solids may be converted into mist by atomizing their solutions in easily volatile liquids which do not themselves form mists, and organic substances in benzene, for instance, may be employed. By changing the concentration of the solution we are also able to change the density of the mist and the size of its particles. A very effective atomizer may be made by allowing the jet of drops issuing from an ordinary atomizer to impinge upon a ground glass plate G (see Fig. 149).

Here also we have the possibility of turning an originally polydisperse mist into one largely monodisperse, or at least of freeing it from all particles above a certain size. According to Regener's proposal, the stream of drops from the atomizer Z (see Fig. 150) is led at sufficient speed through a glass spiral S with close turns.

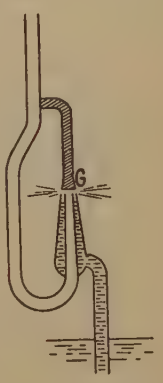


Fig. 149.

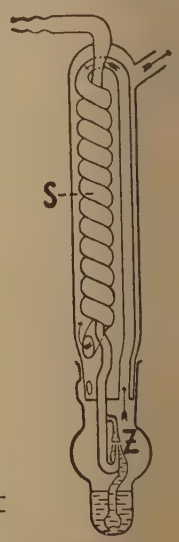


Fig. 150.

[1] This and a number of the following data are drawn from experiments not yet published, the communication of which here has been kindly permitted by Prof. *Regener*.

[2] Phil. Mag. (4), **37**, 384 (1869).

[3] Zeitschr. f. physik. Chemie, **95**, 378 (1920).

[4] *loc. cit.*

By centrifugal force all coarser particles receive such an acceleration that they are deposited on the walls of the spiral. It may be calculated that when the air jet has a velocity of 10 metres per second and the spiral a radius of 1 cm., an acceleration 1,000 times that due to gravity is obtained. A particle of radius 100 $\mu\mu$ which falls in the earth's gravitational field at the rate of 0·003 cm. per second, is thrown on to the wall of the tube by the Regener spiral atomizer at a velocity of 0·3 cm. per second, hence the separation is much more effective than that produced by gravity.

The fact that mist particles may be readily deposited on a wall by motion implies that any kind of motion of a quantity of mist in a vessel may sensibly change the number of particles in it. This is even the case when it is attempted to mix uniformly a mist in a large vessel by means of a mechanical stirrer.

Liquids and readily volatile solids are also turned into mist when embedded in an explosive in a thin-walled vessel and explosion produced.

The Optical Properties of Mist and Smoke

If a mist has drops as uniform as possible, and small compared with the wave-length of visible light, and if these drops consist of an insulating colourless liquid, the Tyndall effect may be observed in a very pure and strong form. Tyndall [1] investigated it particularly upon mists, especially those which he produced, as described above, by photochemical reactions. We have therefore the pronounced polarization of the light scattered sideways, and a colour such as follows from the equation already given on p. 381. It is therefore particularly the light of short wave-length that is scattered sideways; the mist appears blue against a dark background, and reddish yellow by transmitted light. How far the agreement with the theory goes is seen from the following experiment by Bock.[2] He produced a blue jet of water vapour by bringing hydrochloric acid into the jet of steam (see p. 770); and measured spectro-photometrically the following ratios for the intensities red : yellow : green : blue : violet = 1 : 1·5 : 2·9 : 4·4 : 9·8, while the values of $\frac{1}{\lambda^4}$ for the rays 700 $\mu\mu$, 590 $\mu\mu$, 540 $\mu\mu$, 470 $\mu\mu$ and 410 $\mu\mu$ are in the ratios 1 : 2 : 2·8 : 4·9 : 8·5. The agreement would be better if rays of definite wave-length and not spectral zones had been compared. Then it is also possible that in these experiments the mist drops were already in part too large, and hence in the neighbourhood of the wave-length of visible light, which leads to departure from the theory.

The Tyndall meter (see p. 382) may be used for mist and smoke as well as for sols,[3] and the same proportionality is found between the intensity of the Tyndall beam and the content of particles in the mist, assuming that the latter is of uniform grain.[4]

The Rayleigh theory of the Tyndall phenomenon presupposes no lower limit for the size of the particles. It follows from this that the gas molecules must also scatter light. The effect produced by them is considerably smaller than that produced by mist particles, since the intensity of the

[1] *loc. cit.*, p. 774.
[2] Wied. Ann. **68**, 674 (1899).
[3] *Tolman* and *Vliet*, Journ. Amer. Chem. Soc. **41**, 297 (1919).
[4] *Tolman, Reyerson, Vliet, Gerke* and *Brooks*, Journ. Amer. Chem. Soc. **41**, 300 (1919).

scattered light, according to equation (2), p. 381, increases proportionally to the square of the volume of the particles. Hence it is no easy task, with volumes of gas such as are possible in laboratories, to distinguish the Tyndall effect due to the gas molecules from that due to chance particles of mist and dust. With gas spaces as large as that of the atmosphere the Tyndall effect of the molecules can produce a strong effect.

In fact, the colour of the sky depends upon this phenomenon.[1] In support of this we have not only the fact that the sky is blue but that the state of polarization of the light from it behaves like Tyndall light. One might indeed assume that fine drops of water and dust in the atmosphere cause the Tyndall phenomenon. But colour and polarization remain the same when we ascend 2,000 to 3,000 metres in the atmosphere. Under these conditions the layer containing dust in sensible amount is then below the observer. It is still more decisive that the light from the sky also behaves numerically as if it were scattered by molecules and not by mist or smoke particles.

In order to pass from the formula given on p. 381 to one valid for the conditions under discussion, we must take the following relations into account. For the number ν of particles contained in 1 c.c. we have in the first place to substitute the number of molecules contained in 1 c.c., namely

$$\nu = \frac{p\mathrm{N}}{\mathrm{RT}}$$

where N is Avogadro's number, and p the gas pressure. For the expression

$$\frac{n_1^2 - n^2}{n_1^2 + 2n^2}$$

which contains the refractive indices n_1 and n of the particles and gas respectively, we have to put, according to Rayleigh,

$$\frac{n_1^2 - n^2}{n_1^2 + 2n^2} = \frac{2n_0 - 1}{3\nu v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here n_0 is the refractive index of air, ν, as always, the number of particles in 1 c.c., v the volume of the single particle. Finally we have to take into account that in the measurement we are not concerned with the total rays passing into space; the experiment, on the contrary, is carried out by comparing spectrophotometrically the intensity I_0 of the Tyndall light at a point of the sky with the intensity I_e of the exciting light coming from the surface F of the sun. If this is all introduced, we arrive at an equation

$$\frac{\mathrm{I}_0}{\mathrm{I}_e} = \frac{\pi^2 \mathrm{RTF}}{\mathrm{N}px^2\lambda^4}(n_0^2 - 1)^2 \sin^2 a \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which the letters not hitherto mentioned have the same meaning as in equation (2), p. 381. All these quantities can be directly measured excepting N. Hence a measurement of the intensity of light from the blue sky is a new way of determining Avogadro's number. The experiments carried out by E. Bauer and Moulin [2] on Mont Blanc under not very favourable atmospheric conditions gave for N values between about 40×10^{22} and 70×10^{22}; they approach in the mean the reliable value of 61×10^{22}.

This agreement is conversely a proof that the blue colour of the sky is actually due to the Tyndall phenomenon of the air molecules. The mani-

[1] *Rayleigh*, Phil. Mag. (4), **41**, 107 (1871); (5) **47**, 375 (1899).
[2] Compt. rendu, **151**, 864 (1910).

fold colours, especially red and yellow, of sunrise and sunset are naturally due in part to mist and dust particles.

If it were also possible to investigate the Tyndall light of gas molecules under laboratory conditions, we should have a noteworthy method of elucidating the shape of the molecules. For, as already shortly remarked on p. 385, only in the case of perfectly spherical particles is the light scattered at right-angles to the entering beam strictly linearly polarized; the electric vector vibrates at right-angles to the plane in which the path of entry of the light lies. In this plane there is no vector of the light scattered laterally. With non-spherical particles, the intensity I_p of this light also vibrating parallel to the plane of entry is much smaller than that I_s vibrating at right-angles, but still measurable. Strutt [1] has tried to carry out such measurements. He used a very strong arc light falling into a carefully blackened box; the gases investigated were filtered through P_2O_5 and cotton-wool. A very weak Tyndall light was then observed and photographed, the intensity of which did not change when the gas was refiltered through cotton wool, but did so on evacuation of the box. Strutt assumes that this Tyndall light is caused by the gas molecules. Should this prove to be correct,[2] gases differ in a striking manner, which would allow of the following conclusion concerning the shape of their molecules. With pentane, hydrogen, ether vapour, I_p only amounted to 1 to 2 per cent. of I_s. Their molecules would thus be approximately spherical. I_p was larger (3 to 14 per cent.) with chloroform vapour, ethylene, nitrogen, chlorine, carbon dioxide, carbon tetrachloride, benzene, oxygen, carbon monoxide, carbon disulphide, cyanogen, nitrogen peroxide; with these the departure from spherical form would be greater. Helium assumed a peculiar position, having an I_p of 42 per cent., which was excessively sensitive to impurities, so that Strutt considers a value of 50 per cent. not improbable. This would prove correct if the vibrations in the helium atom were strictly confined to a straight line, while in the case of the spherical molecule any direction of oscillation would be equally probable. Naturally the Tyndall light is excessively weak in the case of helium and hydrogen, corresponding to the small size of their atoms or molecules, so that the photographic plates had to be exposed for many hours.

These experiments have been considered at comparative length, not because their results may be regarded as absolutely assured, but in order to draw attention to the fact that the investigation of the Tyndall effect of gas molecules is an important new method of investigating the shape of atoms and molecules and hence of the structure of atoms.

The *opalescence* observed in the neighbourhood of the critical point liquid—vapour may also be referred to the Tyndall effect. It appears in a range of several degrees in the neighbourhood of this point, and is an entirely regular and reversible phenomenon, not caused by impurities.[3] v. Smoluchowski [4] succeeded in explaining it on the following basis. According to the kinetic theory we have, even in pure gases, variations in density, as was

[1] Proc. Roy. Soc. **94**, A, 453 (1918); **95**, A, 155 (1918); (*Rayleigh*) **97**, A, 435 (1920).

[2] See, on the other hand, *Wood*, Phil. Mag. (6), **36**, 272 (1918), and *Strutt*, *ibid.* **36**, 320 (1918).

[3] See particularly *Altschul*, Zeitschr. f. physik. Chemie, **11**, 578 (1893); *Travers* and *Usher*, *ibid.* **57**, 365 (1906); *S. Young*, Proc. Roy. Soc. **78**, 262 (1906).

[4] Ann. d. Physik (4), **25**, 205 (1908).

considered in detail on p. 353 in connexion with the variations occurring in Brownian movement; in a very small volume therefore there will sometimes be a large, sometimes a small number of molecules present. Calculation shows that these chance condensations and rarefactions are the more pronounced the fewer the number of molecules present in the volume in question and the smaller the differential coefficient $\frac{dp}{dv}$. But this is equal to zero at the critical point. Hence at that point the variations in density are much greater than in the region of homogeneous gas and homogeneous liquid. For ethyl ether, for instance, at the critical point, a mean deviation of the density $\delta = 7{\cdot}2 \times 10^{-2}$ can be calculated, while at 20° and normal pressure for ether vapour $\delta = 3{\cdot}7 \times 10^{-5}$. At the critical temperature the variations of density are about 200 times greater. The local condensations of molecules thus produced cause scattering of light exactly like those caused by a foreign particle of different density. The Tyndall phenomenon therefore appears.

Starting from Smoluchowski's considerations, Einstein [1] calculated the intensity of the light scattered in this way, and Keesom [2] was able to confirm the theoretical consequences by experiment. In the first place the intensity of the Tyndall light as compared with that of the entering light was in quantitative agreement with theory. It then appeared, likewise in accordance with theory, that the intensity of the Tyndall light is inversely proportional to the distance of the temperature from the critical point, hence

$$I = \frac{k}{T_k - T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It is true that in the immediate neighbourhood of the critical point sensible departures from this formula occur, inasmuch as the observed opalescence is less than that required by the theory.

It may be remarked that Einstein was also able to show in the same paper that on the basis of these variations in density of a homogeneous gas we reach equation (2), which holds for the Tyndall light produced by the gas molecules.

A mixture of two liquids not miscible in all proportions also behaves at its critical point like a gas. There also a distinct opalescence is observed, which has been especially investigated by J. Friedländer,[3] while Wo. Ostwald [4] proved that equation (3) is again fulfilled. The departure from the formula in the immediate neighbourhood of the critical point was likewise particularly plain in the sense above described.

v. Lepkowski [5] examined the ultramicroscopic behaviour of the mixture amylene-aniline in the region of its critical point of mixture. An extremely strong flickering motion and finally submicrons, which were not, however, limited by sharp outlines, were observed. It is also noteworthy how slowly such chance differences in the liquid are removed by diffusion. The experiment may be commenced by fixing one's attention upon a certain drop at sufficiently low temperature, at which separation into two phases has begun. If we now warm the mixture to such an extent that not only the drop but also the flicker which takes its place disappears, then on

[1] Ann. d. Physik (4), **33**, 1275 (1910).
[2] Ann. d. Physik (4), **35**, 591 (1911).
[3] Zeitschr. f. physik. Chemie, **38**, 385 (1901).
[4] Ann. d. Physik (4), **36**, 848 (1911).
[5] Zeitschr. f. physik. Chemie, **75**, 608 (1910).

cooling the drop, preceded by the flicker, reappears at exactly the same spot, and even with the same outline as before. This phenomenon may be followed even after repeated heating and cooling.

If the particles of a mist or smoke are coarse, and approach or exceed the wave-length of visible light, the mist becomes white. In transmitted light, on account of diffraction and interference, the well-known coloured interference rings and areas are formed, provided that the particles are not too large, and are monodisperse, and uniformly distributed in the mist or smoke. From the diameter of the diffraction rings the size of the particles may be estimated.[1]

A further optical property of white mist is the interference with visibility which it causes. Comparatively small amounts of matter suffice to make an object invisible at 20 metres distance in ordinary daylight; in the case of the most used fog-producer (a mixture of sulphur trioxide with 10 per cent. HCl, which is allowed to drop upon quicklime) about 20 to 25 mg. per cubic metre are sufficient, the radius of the particles being about $500\mu\mu$. With titanium tetrachloride only about 13 mg. per cubic metre are necessary.[2]

Mist and smoke may be examined in the ultramicroscope exactly in the same way as colloidal solutions. Only the slit ultramicroscope has been used for this purpose, since in view of the more rapid rates of fall of mist and smoke particles compared with the micellæ of sols, it is necessary to carry them in a slow current of air from a store chamber through the observation chamber of the microscope. The chamber shown in Fig. 151 *a* and *b* in vertical and horizontal section has proved of value in investigation by Regener.[3] The observation chamber consists of a tunnel A which increases in diameter from the front, and is bored out of a piece of brass B. The observation objective O is directed at an opening H at the side. Both openings are closed by cover-glasses, which must be frequently renewed, since they readily become dirty by precipitation. The air containing mist is led in by the tube C and out by D by suction. The cone G connected to the screw F allows the rate of the air current to be regulated.

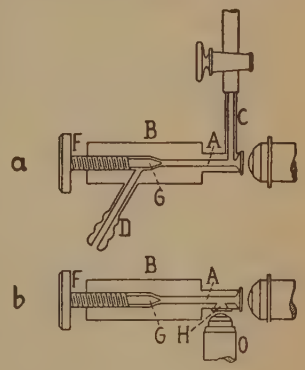


Fig. 151.

The colour of the light emitted laterally from submicrons in metallic mists, as investigated particularly by Ehrenhaft (p. 782), may be explained according to Frl. Laski[4] on the basis of Mie's theory (p. 382). From the

[1] See on this point *Kiessling*, "Untersuchungen über Dämmerungserscheinungen," Hamburg and Leipzig, 1888; *Barns*, Phil. Mag. (6), **4**, 24 (1902); Amer. Journ. of Science, **13**, 81 (1902); **15**, 335 (1903); **22**, 342 (1906) and others; *Bock*, *loc. cit.*, p. 775.

[2] *Regener*, *loc. cit.*, p. 774.

[3] *loc. cit.*, p. 774.

[4] Ann. d. Physik (4), **53**, 1 (1917); Physik. Zeitschr. **19**, 369 (1918); see also *R. Fürth*, Sitzungsber. d. Wien. Akad. d. Wiss. **127**, IIa, 119 (1918).

colour the size of the particles may be deduced, and this agrees for silver particles with a radius of over 40 $\mu\mu$ with the value deduced from the rate of fall.

Senftleben and Frl. Benedict [1] have shown that the considerations of Mie's theory may be successfully applied to luminous hydrocarbon flames. If strong light is allowed to pass through such a flame, a Tyndall effect is observed, and the light scattered laterally may be calculated on the assumption of spherical particles of carbon to which the optical constants of carbon are ascribed.

Brownian Movement and Rate of Fall of Mist and Smoke Particles

For the Brownian movement of mist and smoke particles the same laws hold throughout as were developed on p. 343. Since the viscosity of air is some 50 times smaller than that of water (0·0001824 [2] as against 0·00939 at 25°), the mean transverse and rotatory displacements will be correspondingly larger.

This is likewise evident in the rate of fall of the particles. The Stokes formula (cf. equation (3), p. 344),

$$u = \frac{2}{9}\frac{r^2\ (\varrho_f - \varrho_g)g}{\eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(ϱ_g is the density of air, ϱ_f that of the liquid) no longer suffices for the observations. It assumes that the particles are large compared with the mean free path of the gas molecule, an assumption that will be less fulfilled in the case of gases than of liquids. An improvement in the Stokes formula deduced by Cunningham [3] is frequently used:

$$u = \frac{2}{9}\frac{r^2(\varrho_f - \varrho_g)g}{\eta}\left(1 + \mathrm{A}\frac{l}{r}\right) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here l is the mean free path of the gas molecule, A a constant to which a different value must be ascribed according as we assume that the impact of the gas molecule upon the mist particle is entirely elastic, entirely inelastic, or that a certain fraction only is elastic. A has a value of 0·805 when all molecules are elastically reflected.

According to Weiss,[4] the translatory displacement ξ of a particle in Brownian motion may be calculated from measurements of the rate of fall. One and the same particle is allowed to fall repeatedly, the rate and time of fall determined, and compared with the mean value of a large number of such measurements. Measurements of this kind may be made by following the fall of a particle of gold or silver ultramicroscopically, determining the length of its path by means of an ocular micrometer, raising the particle by means of an electric field and after removing the field allowing the particle to fall again. If x is the distance fallen, u the velocity, t the observed time of fall of a single experiment and t_m the mean time of fall calculated from the experiments, then

$$x = ut_m = ut + \xi$$

[1] Ber. d. deutsch. physik. Ges. **21**, 144 (1919); Ann. d. Physik (4), **60**, 297 (1919); Kolloidzeitschr. **26**, 97 (1920).

[2] According to *Millikan's* measurements, Ann. d. Physik (4), **41**, 759 (1913).

[3] Proc. Roy. Soc. **83**, A, 357 (1910).

[4] Ber. d. Wien. Akad. d. Wiss. **120**, IIa, 1021 (1911). See also *Wells* and *Gerke*, Journ. Amer. Chem. Soc. **41**, 312 (1919), who give the particles an oscillatory motion by current impulses continually alternating in direction, and from their amplitude and the known time for which the current acts, calculate the size of the particle.

hence the mean square of the transverse displacement with n experiments,

$$\overline{\xi^2} = \frac{1}{n} \Sigma \xi^2 = \frac{u^2}{n} \Sigma (t_m - t)^2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The Electrical Properties of Mist and Smoke Particles

In the foregoing description no fundamental distinction has been made between the behaviour of mist and smoke particles and that of the particles in colloidal solutions. As regards the electrical behaviour such a distinction must be made, especially when hydrophobic sols are used for comparison. In these the number of ions is so great, the possibility of their formation so strong, that the micellæ behave as if surrounded by an electrical double layer ; the number of charges carried by a single micella is considerable (see p. 393). They are to a great extent neutralized by an oppositely charged external coating. Hence one cannot determine whether a micella has taken up a charge or lost one, but on the other hand it is possible to ascribe to the micella a definite characteristic charge, and to speak of positive and negative sols. In the gas space, conversely, the number of carriers of electricity originally present is so small, as is also the possibility of their formation, that the particles of a freshly prepared mist are by no means all equally and strongly charged. If the charge is tested by allowing an electric field to act upon the mist and smoke particles, many, being positively charged, move rapidly to the cathode, others, negatively charged, to the anode, others fall, uncharged, in the same way as in the absence of the electric field. It may be observed how a particle alters its charge by taking up one or several electrons. This sometimes happens of itself without external action. It may be caused to take place artificially by increasing the number of gas ions present, say by sending rays from a radio-active substance into the mist.

This phenomenon has become of great importance, since it allows of a determination of the elementary quantity of electricity, the charge of the electron. Millikan[1] has carried out experiments in this way which were confirmed by Regener,[2] Schidlof,[3] and others. He followed ultramicroscopically the movements of single fine drops of paraffin oil, having radii of 250 to 2,300 $\mu\mu$, which fell either alone under the influence of gravity, or under the simultaneous influence of gravity and an electric field, by means of which latter they could also be made to move upwards. The velocity was determined from the time required to move over a certain distance in the observation field of the microscope. If the particles are spherical, the frictional resistance experienced by them is the same whether they move under the influence of gravity alone, or combined with that of the electric field. Now according to equation (4), p. 349, the frictional resistance R is equal to the force acting on the particles divided by their velocity. If the velocity in the gravitational field alone be v_1, then

$$R = \frac{mg}{v_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[1] Phil. Mag. (6), **19**, 209 (1910) ; Physik. Zeitschr. **11**, 1097 (1910) ; **14**, 796 (1913) ; Physic. Rev. **32**, 349 (1911) ; Ann. d. Physik (4), **50**, 729 (1916) ; there also a full bibliography. About simultaneously *Ehrenhaft* [Anz. d. Wien. Akad. 1909, p. 72] made use of this method, although with another result. See *Millikan*, "The Electron," Camb. Univ. Press, 1917.

[2] Physik. Zeitschr. **12**, 135 (1911). [3] Physik. Zeitschr. **17**, 376 (1916).

where m is the mass of a single particle and g the acceleration due to gravity ; and

$$R = \frac{eE - mg}{v_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

when gravity and the electric field both act on the particle ; here v_2 is the velocity, e the charge on the particle, and E the strength of the electric field.

From (1) and (2) it follows that

$$\frac{v_1}{v_2} = \frac{mg}{eE - mg} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If r is the radius of the particles, ϱ_f their density, and ϱ_g the density of the air, then m is obtained from the formula

$$m = \frac{4}{3}\pi r^3 (\varrho_f - \varrho_g) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

while r may be deduced from the Stokes-Cunningham formula (cf. p. 780) on the basis of the rate of fall under gravity. Thus from formulæ (3) and (4), and the Stokes-Cunningham formula, a relation is obtained by which e may be calculated. In it appear both the size and the density of the particle.

The charges thus found were whole multiples of an elementary charge of $4{\cdot}77$ to $4{\cdot}80 \times 10^{-10}$ electrostatic units. The charge on a particle never varied continuously, but only in leaps which consisted of this amount or of multiples of it.

Ehrenhaft [1] carried out experiments of this kind with considerably smaller particles of mercury, silver, gold, sulphur, selenium (they were obtained by evaporation and condensation or by disintegration in the electric arc) and found on the basis of a method of calculation of the kind above given much smaller charges, and he did not hesitate to conclude that there was no such thing as an elementary charge of the size given ; that if one exist, it must be much smaller.

This conclusion is probably erroneous. It is much more likely that circumstances exist which falsify the above calculation of the charge in the case of small particles. It is a matter of the size of the particles. For Radel [2] was able to show that mercury particles, for instance, with a radius of over 150 $\mu\mu$, give a correct value for the elementary charge, smaller ones give smaller and smaller values of it as their radii decrease. But this depends upon some uncertainty or other existing as regards the density [3] or the shape of the small particles. For if one uses for determining the charge e a formula in which the density and shape of the particle do not occur, the correct value of the elementary charge is obtained even with these very small particles. Weiss [4] already reached this result with silver particles, with which, as in Ehrenhaft's experiments, much too small values

[1] In particular Ann. d. Physik (4), **56,** 1 (1918).

[2] Zeitschr. f. Physik, **3,** 63 (1920).

[3] According to later investigations [*R. Bär* and *Luchsinger*, Phys. Zeitschr. **22,** 225 (1921), and a lecture by *Bär* to the Physikerversammlung in Jena, Sept., 1921] all deviations from the true value of the elementary quantum are due to abnormal density of particles. [*Millikan*, in his book "The Electron" (Camb. Univ. Press, 1917), deals with this question fully.—(*Trans.*)]

[4] *loc. cit.*, p. 780 ; further Physik. Zeitschr. **12,** 630 (1911). Then also *Przibram*, *ibid.* **13,** 106 (1912) ; *Fletcher*, Physik. Zeitschr. **12,** 202 (1911) and *v. Smoluchowski*, *ibid.* **16,** 318 (1915).

of the elementary charge were obtained with direct determination of density and radius. Weiss obtains an independent determination of this kind on the basis of Brownian movement as follows. For the frictional resistance we have, according to equation (7), p. 350, the relation

$$R = 6\pi\eta r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

From this formula and equation (9), p. 350, it follows that

$$R = \frac{2RT}{N\lambda^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where λ^2 denotes the mean square of the displacement in unit time (ξ^2 in the formula just named is the mean square of the displacement in time t).

Now equations (1) and (2) (pp. 781 and 782) may be solved in such a way as to eliminate mg, and we then obtain

$$R = \frac{eE}{v_1 + v_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and hence from (6) and (7)

$$e = \frac{2RT(v_1 + v_2)}{EN\lambda^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

an equation in which neither the size nor the density of the particles occurs. But it assumes (see p. 781) that they are spherical; non-spherical particles are orientated in the electric field, and they experience a friction different from that in the earth's field. Further, λ^2 must be determined by the method of Weiss described above (p. 780).

Weiss,[1] Przibram,[2] and Radel [3] determined the mean square displacement λ^2 and hence calculated according to formula (8) the charge of small particles below 150 $\mu\mu$ radius, which give values which are too low when the method of calculation on p. 782 is employed. Larger constant values, in agreement with the correct one of $4{\cdot}80 \times 10^{-10}$, were then obtained also for the small particles.

Small particles therefore behave as if they were less dense and sensibly larger than one would suppose them to be if they consisted solely of the substances in question, such as mercury. This may perhaps depend upon the fact that with these small drops the adsorption of the surrounding gas plays a larger part, since the surface is comparatively much larger. If this is correct, in a helium atmosphere the ultramicroscopic values should also give a correct value of e from equation (1), since helium is so weakly adsorbed (cf. p. 120).

The first and not very exact values of e were obtained by J. J. Thomson,[4] who likewise used mist, but employed a macroscopic method. In a saturated vapour to which a known electrical charge was imparted, a mist was produced by adiabatic expansion. If the number of drops in the mist are known, and the assumption is made as a first approximation that every single charge collects a drop upon it (which is not the case), then division of the charge by the number of drops gives the single charge and hence e. In order to obtain the number of drops, the size of a drop and the total weight of condensed liquid are determined, the former from the rate of fall of the mist according to Stokes' formula.

[1] *loc. cit.* p. 782. [2] *loc. cit.* p. 782. [3] *loc. cit.* p. 782.
[4] Phil. Mag. (5), **46**, 528 (1898).

Some qualitative results, obtained by C. T. R. Wilson [1] in following the ionization by α, β, and γ rays in supersaturated water vapour on the basis of the formation of mist on sudden expansion, are worth mentioning. An α particle shows a sensibly straight, sharply defined, and hence readily photographed track of mist which at a point near the end of the range of the α particle sometimes shows a sudden change of direction at an acute angle. The α particle has in its course approached a positive nucleus so closely that it has experienced a strong deviation. The path of a β particle is irregularly bent and spattered with drops of mist, since in accordance with its lower mass it is more easily deviated and ionizes more weakly. A γ-ray gives no sharply marked path ; in its passage through supersaturated vapour innumerable irregularly bent short paths radiating out on all sides are produced. They are the paths of the secondary cathode rays produced by the γ-ray, and which have an ionizing effect.

The Stability of Mist and Smoke

The stability of a mist may be influenced in two directions : the drops may evaporate, the colloidally disperse structure changes into one molecularly disperse, an expression which is much more justified for gases than for solutions (see p. 531) ; or the drops become larger and sink more rapidly to the bottom. In the case of smoke—as earlier with colloidal solutions—we are usually concerned with the second possibility, while with mist the first deserves attention under some circumstances. Thus Frankland [2] observed that the London fog, notorious for its stability, evaporates very slowly, even when the surroundings are far from saturated with water vapour ; a hygrometer indicated a sensible degree of dryness in a space filled with fog. This arises from the fact that the fog particles are enveloped in soot and other distillation products of coal combustion, which greatly retard evaporation. As is well known, except in a high vacuum, the velocity of evaporation may be referred to a diffusion velocity (see p. 146). Immediately at the surface of the liquid we have a layer of saturated vapour, between this and the unsaturated surrounding space a diffusion gradient, and the rate of evaporation depends upon the rate of diffusion through this layer. A thin layer of oily contamination or of soot and the like suffices to hinder the formation of the saturated layer. Frankland readily demonstrated with an extended water surface that the velocity of evaporation is depressed by slight contamination to a fraction of that observed with a clean surface.[3]

Mist and smoke settle under the influence of gravity more quickly than the particles of a colloidal solution, since the rate of fall is larger. Drops of water mist, with particles of a radius of 400 $\mu\mu$, already attain a rate of fall of 0·003 cm. per sec., and hence settle under laboratory conditions in a short time ; a distance of 10 cm. is covered in about 40 min. For comparison, it may be noted that, when suspended in water, particles of the same size and with the same difference 1 in density take more than 3 days to settle by the same amount. For meteorology, questions of the rate of settling of mists, and the growth of mist-drops to rain-drops, are of importance. The relations are very diverse, since one has to deal with locally

[1] Proc. Roy. Soc. **85**, A, 285 (1911) ; **87**, A, 277 (1912).
[2] Proc. Roy. Soc. **28**, 238 (1878–79).
[3] See also *Knudsen*, Ann. d. Physik (4), **47**, 697 (1915).

varying conditions of temperature and supersaturation and with mist nuclei of different kinds.

That in the streaming of gas containing mist through spiral tubes, accelerations may be reached which far exceed those produced by gravity, and that in this way mist and smoke may be freed from coarser particles, was already mentioned on p. 774.

It is at first surprising that under many experimental conditions mist and smoke appear to be influenced much less than many gases. Thus by means of a layer of coarse-grained wood charcoal (particles about 1 mm. diameter) serving as a gas filter, a gas such as chlorine may be held back quantitatively for several minutes, even when the air contains several volumes per cent. of the gas, while smoke, such as that from a cigar, or the mist of sulphur trioxide and many organic liquids, can pass through without serious diminution in content ; further, for a certain size of particle there exists a maximum permeability ; with a larger size of particle it decreases again. This appears from Table 190. A gas-mask canister such as was used in the German army during the war served as filter ; it had a so-called "Schnappdeckel," that is, a thin filter layer consisting of paper. The latter protects better than the charcoal against mist. The rate at which the air containing mist was passed through the canister amounted to about 30 litres per minute. The mist consisted of diphenylarsine chloride, a substance solid at ordinary temperatures and easily turned into mist, for instance by atomizing its solutions in organic solvents. The table allows the maximum permeability with a certain size of the mist droplets to be seen.

TABLE 190

Dependence of the Filtration of a Mist upon the Size of Particle

Radius of the Mist Particles in $\mu\mu$.	Percentage of Mist passing through the Filter.
Under 50	52·4
50–100	87·6
100–200	93·9
200–400	30·4
400–800	4·2
Over 800	0·0

This is certainly a consequence of the combined action of various circumstances. The heavy mist drops will move more in the path of the gas stream than the lighter gas molecules, just as a large ship upon a stream follows the main current uninfluenced by waves and single currents, while small floating objects, driven by the latter, more easily reach the shore. On the other hand it must be remembered that the coarser mist drops are not so much held back by an actual sieve action ; for, according to unpublished experiments by Weigert, short fibred, strongly pressed filters hold them back to a smaller degree than long-fibred, not so strongly pressed ones. Probably the action of these filters depends upon the formation in a long-fibred filter of spiral paths, which act like the spiral tube in the atomizer on p. 774. The coarser particles are accelerated more strongly

and thrown against the walls of the filter canals more violently than the medium-sized particles.

The well-known fact that sal-ammoniac smoke may be bubbled through water has a similar explanation. The translation of the particles in the single bubbles is so slight that only a small part of them reaches the boundaries of the bubbles in the short time of passage of the bubble through the liquid.

Smoke and mist particles may be effectively removed from a gas space by means of an electrical field of high tension. If one electrode is a point, sufficient carriers of electricity are emitted by it to charge the particles, which then move towards the other electrode, where they collect and precipitate. This method, long ago proposed, has recently been worked out technically on a large scale by Cottrell.[1] The difficulties to be overcome consisted particularly in the choice of suitable point electrodes. Voltages of about 100,000, with an intermittent direct current produced by transforming alternating current, are mostly used. The method serves not only to remove smoke particles from furnace gases and thus to mitigate the smoke nuisance, but not less to separate reaction products appearing in mist form, for instance, in the manufacture of sulphuric acid.

Light may also influence the stability of mist or smoke in so far as it is able to set the particles in motion and drive them against the wall. Two influences must be distinguished. In the first place the *pressure of radiation* takes effect in the sense of driving the particles in the direction of radiation. As is well known, Arrhenius [2] explains from this point of view the deflection of the tails of comets by the radiation of the sun, and Nichols and Hull [3] showed how fine soot falling in a vacuum may be deflected from a vertical path by the action of powerful light. Besides this deflection in the direction of the radiation, *positive photophoresis*, Ehrenhaft,[4] who has investigated these processes closely, particularly on submicrons, observed a *negative photophoresis* ; submicrons of sulphur, selenium, and other substances in pure argon moved upon illumination against the light. According to Rubinowics [5] and Frl. Laski and Zerner,[6] this negative photophoresis depends upon a *radiometer effect*. With strongly absorbing particles the side turned towards the light is heated more strongly than that away from the light ; the radiometer action moves them in the same direction as the radiation pressure. With more weakly absorbing substances, such as sulphur and selenium, the refraction of the light in the particles may cause them to be warmed more strongly on the side away from the light, and a negative photophoresis follows. The fact, which is at first surprising for a radiometer action, that negative photophoresis is, according to Ehrenhaft, independent of the gas pressure, was deduced by Frl. Laski and Zerner from the theory.

Together with all these general radiometer actions a coarser one can be distinguished when the particles, at first unsymmetrical, are for instance

[1] See report of the Smithsonian Inst., 1913, p. 653. Concerning many technical questions connected with mist and smoke, see *Kohlschütter*, "Nebel, Rauch, und Staub," Berne, 1918.

[2] Physik. Zeitschr. **2**, 81, 97 (1900).

[3] Astrophys. Journ. **17**, 352 (1903).

[4] Physik. Zeitschr. **18**, 359 (1917).

[5] Ann. d. Physik (4), **62**, 691, 716 (1920).

[6] Zeitschr. f. Physik, **3**, 224 (1920). But see *Ray*, Ann. d. Phys. (4), **66**, 71 (1921).

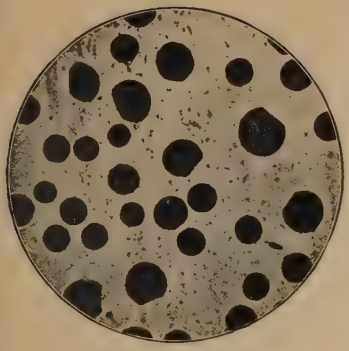


FIG. 152.

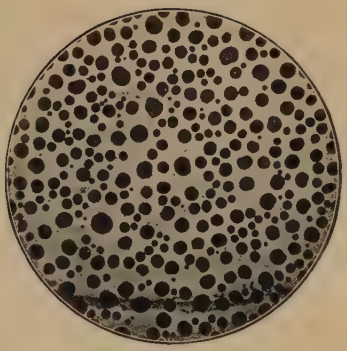


FIG. 153.

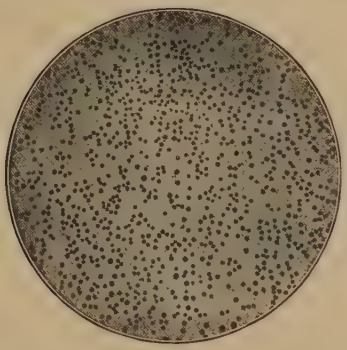


FIG. 154.

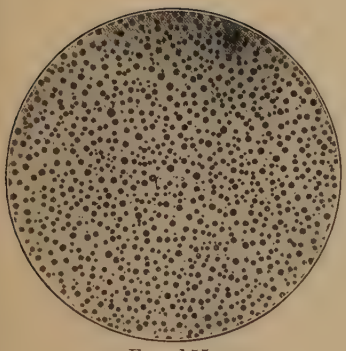


FIG. 155.

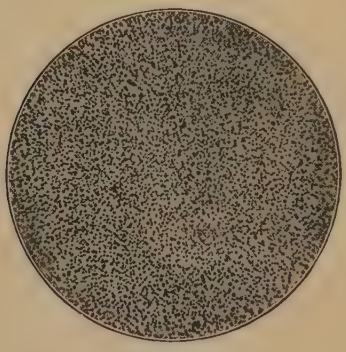


FIG. 156.

To face page 786.]

changed at one point by chemical attack, so that opposite sides are warmed to different degrees. Thus in the case of the mist of diphenylarsine chloride above mentioned it was observed that, while its particles were mostly uninfluenced by light, some strongly susceptible to photophoretic influence appeared when they had been chemically attacked by too strong heating.[1]

The Separation of Liquid and Solid Substances from Mist and Smoke

The forms in which substances separate from mist and smoke are scarcely less diverse than those in which solids separate from sols. Kohlschütter and Ehlers [2] examined substances such as arsenic, selenium, zinc, and cadmium by allowing them to evaporate *in vacuo* or in various gases at different pressures, and collected the deposits from the vapour upon object glasses under conditions as comparable as possible. The microscopical investigation [3] showed that the deposit produced *in vacuo* is coarsest; it becomes more and more disperse the higher the gas pressure and the denser the gas used. On Plate VII are given the forms of separation of zinc, in Fig. 152 in hydrogen at a pressure of 5 cm. Hg; in Figs. 153 and 154 in hydrogen and nitrogen at 30 cm. Hg; in Figs. 155 and 156 in the same gases at 70 cm. Kohlschütter explains this behaviour as follows. The larger the number of gas molecules and the heavier they are, the more lively the Brownian movement of the mist and smoke particles first separating; and the more lively their movement, the more does it oppose the surface tension or cohesive forces, which strive to form larger drops or crystals from the smallest particles.

Connected with this phenomenon is the fact that metals sometimes separate in hair-like crystals, silver, for instance, as hair-silver. According to Kohlschütter and Eydmann,[4] this happens when silver is formed in a comparatively dense vapour, such as that of silver sulphide, and only comes into contact with isolated silver nuclei. In the dense vapour the silver is retained to a pronounced degree as highly disperse mist, and separates gradually upon the single nuclei present, for instance, upon the walls. In accordance with this is the fact that hair-selenium [5] was observed at atmospheric pressure (not below it) and in heavy gases such as CO_2 and SO_2, and not less the fact that nickel separates from gaseous nickel carbonyl as a woolly felt of hair-nickel.[6]

Reinders and L. Hamburger [7] have extended these results in a noteworthy manner. They evaporated metals and also other substances, such as NaCl and CaF_2, by using the former as filaments in electric lamps, and

[1] *Regener, loc. cit.*, p. 774.

[2] Zeitschr. f. Elektrochemie, **18,** 373 (1912).

[3] *Reinders* and *L. Hamburger* [Koninkl. Akad. v. Wetensch. Amsterdam, **19,** 958 (1916)] found that precipitates of gold and silver produced by vaporization and condensation appeared under the ultramicroscope to be colloidally disperse.

[4] Lieb. Ann. **390,** 340 (1912).

[5] *Kohlschütter* and *Ehlers*, Zeitschr. f. Elektrochem. **18,** 377 (1912).

[6] According to observations by *Zisch.* The formation of hair crystals observed in the drying up of gels containing in solution substances tending to crystallize has other causes; a SiO_2 gel containing NaCl may be given as an example. Here it is doubtless a matter of the formation of spatially separated crystal nuclei which are situated at the mouths of pores, and are fed there from the supersaturated solution contained in the pores, while the gel shrinks.

[7] Koninkl. Akad. v. Wetensch. Amsterdam, **25,** 661 (1916); **26,** 595 (1917); *L. Hamberger,* Kolloidzeitschr. **23,** 177 (1918).

by coating difficultly volatile filaments of tungsten with the latter. Since the precipitates altered when they came in contact with air and moisture, they were fixed while still in the vacuum of the glow-lamp by a coat of Canada balsam or of CaF_2 produced by the evaporation of this substance. It was found that it is possible not only to obtain layers which may be resolved microscopically and ultramicroscopically, but also optically irresolvable deposits. Such irresolvable deposits consist of supercooled melts of the substances in question. They were not only observed with salts such as NaCl and CaF_2, but also with metals ; especially the metals or elements of high melting-point, such as W, Mo, Pt, Fe, Ni, C ; much less with Au, Ag, Cu, Hg, Zn, Cd, although these also gave along with submicrons parts of the layer which were optically irresolvable and so doubtless supercooled. This circumstance may perhaps also be called in to account for the irregular behaviour of very small particles observed by Ehrenhaft (see p. 782). For the production of the supercooled melt it is favourable when the wall on which condensation takes place has a temperature as far below the boiling-point of the vaporizing substance as possible ; here also the vapour pressure is low and hence also the tendency to form larger particles. Hence in the optically irresolvable tungsten layers atom lies uniformly against atom. With this agrees the fact that in the case of tungsten the electrical conductivity of the layer is already sensible at a thickness of 0·5 $\mu\mu$, and increases rapidly at 2·5 $\mu\mu$, while in the case of silver, which has a strong tendency to coarsen, and the layers of which are therefore less continuous, the corresponding figures were 6·5 $\mu\mu$ and 25 $\mu\mu$.[1] Hamburger got the impression that unimolecular layers of the supercooled melts are comparatively stable, while the tendency to the formation of coarser particles increases as the layer becomes thicker, a behaviour like that of oil films (cf. p. 312).

The observed colour phenomena, as known from other colloido-chemical phenomena, may be suitably discussed here. As the layer becomes thicker the colour changes by transmitted light in the case of gold from rose through red, violet, and blue to green, with silver from orange-yellow, through red and violet to blue (see p. 385). If the vaporized metal is allowed to deposit upon a suitable layer, say that of a salt, it may happen that the single atoms of metal penetrate into the interior of the salt, hence do not form a continuous layer, and have no possibility of associating to coarser particles. Such layers containing metal prove to be colourless ; we have as it were a colourless solution of the atomically dispersed metal (see p. 800).

Similar circumstances come into play in the metallic layers obtained by cathodic disintegration.[2] The layers are found to be disperse under the ultramicroscope. If Ag layers are investigated in the gases H_2, N_2 and Ar with H_2 the smallest and with Ar the largest amount of metal is necessary to produce a given resistance over a given area. This arises from the fact as just described, that in hydrogen the metallic layer is more continuous than in the denser argon. The resistance decreases in time, as the metal becomes more coarsely disperse, and hence more continuous. With H_2 it may attain high values again of itself, with the other gases on heating since this coarsening sometimes completely tears the layer, so that unbridgable parts of high resistance are formed. It is noteworthy that this gradual coarsening, betrayed by the decrease in resistance, may be checked if the

[1] *S. Weber* and *Oosterhuis*, Koninkl. Akad. v. Wetensch. Amsterdam, **25**, 606 (1916).

[2] *Kohlschütter* and *Noll*, Zeitschr. f. Elektrochemie, **18**, 419 (1912).

layers are kept at a pressure of 10 to 70 cm. Hg in N_2 (e.g.) instead of one of 0·02 to 0·03 cm.; the denser gas and the higher pressure thus check the coarsening just as, in the case of a colloidal solution, this effect is produced by strongly increasing the viscosity of the dispersion medium.[1]

The differences in the degree of dispersion also take effect in the catalytic activity of the layers; in argon a platinum mirror of 2 mg. weight could be made of such activity, that upon passing hydrogen mixed with air over it, water dripped off it continually, while a layer of the same weight produced in hydrogen did not cause any sensible amount of water to be formed in a considerable time.[2]

The tendency towards reduction of the degree of dispersity appears with many highly disperse oxides, such as Cr_2O_3, Fe_2O_3, ZrO_2, and others in the curious *glowing* which they show upon being heated up to temperatures of a few hundred degrees. Berzelius already observed it and regarded it as a change to an allotropic form. L. Wöhler [3] renders it very likely that it is simply a rapid coarsening, in which the heat set free suffices to raise the temperature of the oxide by 50 to 100° and to cause it to become incandescent. In favour of this is the fact that everything tending to make the oxide highly disperse increases the heat developed.

C. FOAMS

Foams are disperse structures with a liquid as dispersion medium and a gas as disperse phase. Those with which we are usually concerned differ from the structures hitherto discussed in that the disperse phase, the gas, is present in the form of macroscopic bubbles, while the liquid lamellæ separating them are of micronic or submicronic thickness. Hitherto the disperse phase was always submicronic or amicronic, and, except in the case of gels, thick layers of the dispersion medium separated the particles. This does not mean that these properties are essential to foams; it is entirely probable that foams also exist in which the gas bubbles are submicronic or amicronic, thus perhaps many froths occurring with froth-producing living organisms.

Preparation and Capillary Chemical Conditions of Stability of Foams

A foam is in every case a labile structure. So large a surface development is always in contradiction to the rule that as a consequence of the surface tension the surface tends to the smallest possible size. This is true for other disperse structures, such as a colloidal solution, only that there the kinetic energy of the molecules exerts a counter-effect, so that true equilibria are possible. Such a kinetic counter-effect is absent in the case of foams. Hence they are subject to a continual change with time in the sense of a diminution of surface.

A further consequence is that a whole series of special conditions must be fulfilled in order that a fairly permanent froth may be obtained. We

[1] Regarding further, older investigations of the change in conductivity of thin layers of metal, see *Oberbeck* [Wied. Ann. **46,** 265 (1892); **47,** 353 (1892)]; *Grimm* [Ann. d. Physik (4), **5,** 448 (1901)]; *Fawcett* [Phil. Mag. (5), **46,** 500 (1898)]; *L. Hamburger* [Kolloidzeitschr. **23,** 192 *et seq.* (1918)].

[2] *Kohlschütter* and *Noll*, Zeitschr. f. Elektrochemie, **18,** 419 (1912).

[3] Kolloidzeitschr. **11,** 241 (1912); further *Endell* and *R. Rieke*, Zentralbl. Mineral. u. Geol. 1914, p. 246.

may say with certainty that a pure liquid never gives a stable foam. In order that so large a development of surface may be possible, the surface tension must be small. Pure liquids with low surface tension are never far removed from their boiling-points, and hence have a high vapour pressure, thin lamellæ of liquid hence evaporate too quickly even when formed. Pure liquids with a sufficiently small vapour pressure have too large a surface tension. Only capillary-active solutions unite both properties. In actual fact all solutions of capillary-active organic substances in water foam more or less strongly.

But the fulfilment of these conditions does not suffice for the production of durable froths, such as are known in the case of solutions of soap, saponin, many proteins, and other substances. These are all colloidal or semi-colloidal solutions which have a high power of forming tough or amorphous-solid surface films (see p. 749), and this circumstance is decisive for the formation of durable foam.[1] We may therefore picture the formation of a foam somewhat as follows. When an air-bubble passes through the liquid in question, it clothes itself on account of adsorption with a surface film, and at the moment when it is about to leave the liquid, it raises the film already existing at the surface and stretches part of the liquid to a lamella, upon the surface of which the tough film is again formed. In order that the lamella may be stretched at all, the vapour pressure and surface tension must be sufficiently small; but that it lasts so long depends upon the presence of the surface films, which produce a more or less solid skeleton. They further produce the effect that the liquid evaporates much more slowly than from a clean surface (see p. 784), and that the liquid between the two surfaces of the lamella only moves downwards under the influence of gravity very slowly. The friction is, indeed, very great, for the velocity with which the liquid moves in a capillary according to Poiseuille's law is proportional to the fourth power of the radius and hence very small in view of the excessively small thickness of the lamella. The actual viscosity of the liquid in mass will also be unquestionably of importance; a large viscosity is favourable to the stability of the foam.

The peculiarities of surface films will not only appear in the various degrees of stability of the foam, but also in a series of other properties; whether a foam consists of large or small bubbles, whether the bubbles are elastic or rigid, and other properties, will depend chiefly upon peculiarities of the films. Soap solutions are distinguished by their permitting the formation of very elastic bubbles, which, whether small or large, show a quite smooth, flexible surface. It would be a matter of experiment to test whether this is connected with the fact discussed on p. 724, that the gels and coagels separating from soap solutions have elongated, flexible micellæ. The surface films have, as is immediately obvious, the same property of being drawn into threads as the soap jellies in mass. As opposed to this, the bubbles of saponin solutions are much more rigid.[2] If the air be quickly sucked out of a saponin bubble blown upon a pipe, it sinks together to a crinkled bag, which, when the air is drawn out still further, shows folds,

[1] The theory of the formation of foam is due chiefly to *Plateau*, "Statique des Liquides," II, p. 41 *et seq.* (1873), and *Quincke*, Wied. Ann. **35**, 589 *et seq.* (1888); see further particularly *Gibbs*, "Thermodynamische Studien," Leipzig, 1892, p. 351 *et seq.*

On the adsorption of saponin in froth of saponin solutions see *Stortenbeker*, Chem. Weekbl. **7**, 264 (1910).

[2] *Boys*, "Seifenblasen," Leipzig, 1913, pp. 82–83. No reference to this is contained in the English edition.

but upon being blown out again, again becomes a smooth sphere. This process may be repeated several times. The addition of glycerine, which is recommended in many directions for the preparation of good soap solutions, is not only favourable in so far as it increases the viscosity of the liquid in mass, but also because it makes the surface films soft and flexible. This is also evident from the fact that the rigidity of saponin films is likewise greatly reduced by glycerine; saponin solutions containing glycerine approach without attaining the properties of soap solutions.

Coarser and very rigid particles present in the surface apparently only suffice to allow unstable foams with small bubbles to be formed. It is by no means necessary that the small solid particles collected on the surface should have come from the solution itself. They could very well have been introduced on the surface as a difficultly wettable powder. Thus foams with small bubbles are intentionally formed in the flotation method mentioned above (p. 161); the water coated with oil has the small surface tension and low vapour pressure necessary; the finely powdered and in part difficultly wettable ore which, in consequence of the equal value of the surface tension, spreads evenly over the whole surface, produces as it were a solid film, in that the mobility of the liquid between the particles of ore is greatly diminished. When, by the way, we have been speaking of surface films, we should not only consider excessively thin layers of gel, such as were discussed earlier (p. 749); for it is naturally also possible that the coagulation of the adsorbed colloids on the surface leads to the formation of discontinuous coarser flakes, which then, however, in a similar manner to the powder just discussed, may cause the foaming power. Elastic foams with large bubbles will doubtless only occur when the surface films consist of thin homogeneous gel layers.

All circumstances which are favourable in this sense to the formation of foam must also favour the formation of emulsions, as is actually the case (see p. 606). In this case also an adsorption must be present, the formation of a surface film, which is tough and hinders the coalescence of the particles. Coarser powders which adhere to the interface may also replace in part interfacial films formed from the liquid.

The influence exerted by electrical effects has hardly been tested. A series of circumstances may be active: the charge of the solid particles against the liquid, their charge against the gas, and the charge of the liquid against the gas. Probably we are concerned more and more with the electrokinetic potential ζ, and less with the phase boundary force ε, and hence, as far as the gas plays a part, with balloelectric phenomena. The electrical influences are perhaps less directly than indirectly concerned with the stability of the foam; they determine the phase boundary which the particles enter, and the degree to which they are coagulated and hence change the fine structure of the foam.

How dissolved substances influence the formation of foam has not yet been examined in detail in well-characterized cases. The behaviour of capillary-active substances appears to be fairly definite. We must also take into consideration the displacement of foam-forming substances from the surface by capillary-active foreign substances. If the capillary-active foreign substance is able to form surface films and hence to assist foam formation, the liquid will retain its foaming power, but the froth will assume the peculiarities due to the active foreign substance. We have such a case when saponin is added to a soap solution. A soap solution has under comparable concentrations a smaller surface tension than a saponin solution;

hence soap displaces saponin. Boys [1] mentions an experiment in which one drop of a soap solution added to 30 grams of a saponin solution sufficed to abolish the peculiar sack-like shrinkage of saponin bubbles mentioned on p. 790. After the addition of three drops the surface film was readily mobile and elastic, as with bubbles of pure soap solution. Upon this also depends the fact that substances such as soap and saponin may prevent the separation of ore particles by flotation; they occupy the surface of the froth and thus hinder the collection there of hydrophobic ore particles, which are to be separated from the hydrophilic gangue.

If the capillary-active substance is not able to form surface films, it destroys the froth-forming power of the original substance more or less completely by displacing it. This is the reason why saponin solutions containing isobutyric acid do not give durable foams. They do so, however, when the isobutyric acid is neutralized, since we then have the surface-inactive salt in solution instead of the surface-active acid. That a saponin solution loses the power of foaming upon addition of alcohol depends only in part upon displacement; the fact that saponin forms true solutions in alcohol, and hence in this does not form surface films, plays a chief part. The curious phenomenon first described by Quincke,[2] that ethyl ether in minute amounts destroys frothing power (it is sufficient to open an ether bottle in the neighbourhood of a glass of beer covered with froth, in order to destroy the latter immediately) doubtless again depends upon a displacement of the substance forming froth by the surface-active ether.

The question of the formation of a good durable foam with not too small bubbles plays an important part in the production of beer. Hence the majority of investigations on the formation of foam have been undertaken on this liquid, which is not exactly simple from a colloido-chemical point of view. The power of foam-formation is measured by shaking the beer in high, cylindrical, calibrated vessels in a regular manner, and determining the time required for the foam to fall together by a definite amount. According to recent investigations of Windisch and Bermann,[3] a number of substances are concerned in the quality of the froth. Proteins are the actual foam-producers. They lower the surface tension and cause the formation of surface films. But they do not apparently suffice to make the froth sufficiently durable. Other colloids in beer, wheat gum and other dextrin-like substances, are important. These doubtless act in the first place by increasing the viscosity, and then perhaps by causing the surface films to be softer and more elastic, as glycerine does (see p. 791). Perhaps the proteins alone also give too coarse flakes, while the presence of the other substances causes a finer-grained separation and hence a more elastic surface film.

Saponins are employed to give "minerals" and similar drinks frothing properties. Very small amounts suffice. A solution containing 0·01 g. saponin per litre froths very strongly. That such small amounts suffice is intelligible when we consider that, in consequence of adsorption, they are almost completely attracted to the surface.

[1] *Boys*, p. 84 of "Seifenblasen," *loc. cit.* p. 790.
[2] Wied. Ann. **35,** 593 (1888).
[3] Wochenschr. f. Brauerei, **36,** 319 (1919); **37,** 109, 121, 129, 137, 145, 153 (1920).

The Mechanical Properties of Foam Bubbles and Lamellæ and their Influence on the Durability of Foams

The mechanical properties of the lamellæ and of single foam-bubbles are of decisive influence upon the durability of foams.[1] We have first to consider the influences acting upon the thickness of the lamellæ. When a gas bubble rising out of the liquid takes a comparatively thick lamella of liquid with it, excess of liquid at first flows off rapidly under the action of gravity. The velocity of flow, however, decreases rapidly as the thickness of the lamella decreases, since, as pointed out above, the quantity of liquid flowing out of a capillary tube in unit time is proportional to the fourth power of the radius. Gibbs [2] has calculated the velocity with which the liquid moves downwards in a lamella, by putting the process equivalent to the flow of a liquid between two parallel plates. Table 191 gives the values obtained.

According to this, the rate at which the liquid flows away at micronic thickness, and hence the rate of change of the lamella, is small. But if we consider a vertical lamella of soapy water spread out over a wire ring, we find that the decrease in the thickness of the lamella obviously takes place much more quickly, as we can easily recognize from the appearance of the interference colours. This is, as Gibbs [3] was the first to remark, a consequence of the surface tension. The place where the lamella touches the wire appears in section as shown in Fig. 157. Immediately at the wire, the section of which is represented by *a*, the lamella spreads out at *c*, and is

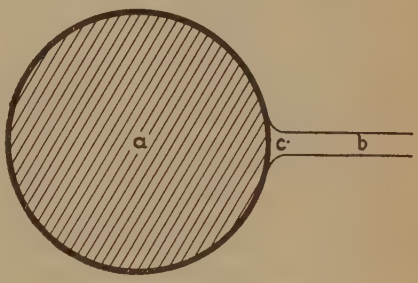


Fig. 157.

Table 191

Rate of Flow of a Liquid out of a Lamella

Thickness of Lamella in mm.	Rate of Flow.
0·01	0·01 cm./sec.
0·001	0·00028 cm./sec. or 0·167 mm./min.
0·0001	0·000019 cm./sec. or 0·278 mm./hour.

there limited by surfaces which are concave outwards with small radii of curvature. The surface tension tends to diminish the surface as much as possible, hence to diminish the curvature by collecting liquid at *c*; liquid is accordingly sucked from the inside of the lamella *b* towards *c*, and the thick-

[1] A detailed discussion in *Plateau's* "Statique des Liquides," vol. II, p. 108 *et seq.*
[2] Scientific Papers, Vol. I, p. 307. Recalculated by *Boys*, "Seifenblasen," p. 126, *loc cit.* p. 790.
[3] Scientific Papers, Vol. I, p. 309.

ness is thus diminished. This is the cause, as shown by direct observation, of the rapid change in the thickness of the lamella.

Gibbs has rightly pointed out how curious it is that a vertical lamella, say in a ring, holds together at all. If the surface tension is everywhere alike, the middle parts will be pulled just as strongly upwards by the parts above as downwards by the parts below. They should therefore sink downwards on account of gravity; but nothing of the kind is observed. This probably depends upon the fact that by such sinking the active substances present on the surface are pressed together below, while the upper part of the lamella becomes poorer in them. Hence the surface tension is a little larger above than below, and this slight pull upwards counterbalances gravity.

It may be remarked that this shows us how little a soap lamella is suited for the experiment mentioned above on p. 6, in deducing the conception of surface tension. When such a lamella is stretched, the surface tension by no means remains constant; it may increase on account of the decrease in the surface concentration of active material.

Evaporation will usually only influence the durability when the foam lamella is in dry air.

What effect does the thinning of the lamella have, and what is the limiting thickness finally attained? The phenomena concerned may be followed either upon lamellæ, the surfaces of which are vertical, the causes of the thinning being gravity and surface tension; or, as is perhaps more convenient, from the decrease in thickness produced by centrifugal force, as was done by Rickenbacher.[1] The lamella is spread out in a horizontal plane upon a drum, which can be rotated about a vertical axis. The decrease in thickness is shown by the appearance of interference colours. They depend upon the interference of light reflected from the front and back surfaces of the lamella. A simple theory of these colours is to be found in Boys' book.[2] The lamella, originally whitish, passes, as its thickness decreases, through the colours greenish-blue, red, and yellow, which, as colours of a higher order, are fairly dull, finally becoming very brilliant as colours of the first order. Since more light is reflected the greater the angle of incidence, the colours are particularly beautiful when the lamella is illuminated from the side. Boys gives a table of colours, by means of which the apparent thickness of the lamella may be determined from the colours seen with a particular angle of incidence, and a table of factors for converting this apparent thickness into the true thickness.

If the lamella—we will still deal only with lamellæ of pure or glycerine soap solution—becomes still thinner, the curious and frequently investigated *black spots*[3] appear, which spread out and under certain circumstances occupy the whole lamella. The thickness of the films has been determined in various ways, either by measuring the electrical conductivity,[4] or by an optical method,[5] for example, the displacement in the

[1] Kolloidchem. Beihefte **8**, 139 (1916).

[2] See also *Reinhold* and *Rücker*, Phil. Trans. **172**, 447 (1881).

[3] They have been particularly investigated by *Reinold* and *Rücker* in the following papers;—*Rücker*, Nature, **16**, 331 (1877); **28**, 389 (1883); Journ. Chem. Soc. **53**, 222 (1888); *Reinold* and *Rücker*, Proc. Roy. Soc. **26**, 334 (1877); **31**, 524 (1881); **40**, 441 (1886); Phil. Trans. **172**, 447 (1881); **174**, 645 (1883); **177**, 627 (1885); **184**, A, 505 (1893); Phil. Mag. (5), **19**, 94 (1885).

[4] *Reinold* and *Rücker*, Phil. Trans. **174**, 645 (1883).

[5] *Reinold* and *Rücker*, *loc. cit.* under [3]; also *Drude*, Wied. Ann. **43**, 158 (1891); *Johonnott*, Phil. Mag. (5), **47**, 501 (1899).

interference fringes of light which has passed through a series of black lamellæ. In measuring the thickness by means of the electrical conductivity the assumption must be made that the specific conductivity of the thicker part of the lamella—the coloured part—is equal to that of the black part. But this is only approximately the case when the soap solution contains a considerable quantity of a foreign electrolyte, such as potassium nitrate : only then do the thicknesses measured electrically and optically agree, the values obtained being between 5 and 15 $\mu\mu$.[1] With solutions poor in electrolytes the conductivity increases considerably in the thinnest part of the coloured film during transition to the black film.

It may be regarded as certain that this black film is materially different from the thicker lamellæ, and it probably consists, as Rickenbacker [2] suggests, simply of the tough jelly-like surface film, which renders possible the formation of foam ; it is quite possible that between the films there is no liquid present at all. These films are again, as we have said, none other than the ordinary micellæ, probably composed of neutral (or acid) soap, which are observed when a soap solution sets to a gel, and the long-fibred form of which has frequently been emphasized (see p. 724). Since the conductivity of the surface film rich in soap is greater than that of the solution, this explains why the conductivity of the solution increases in the transition to the black spot, while this difference is blotted out when the solution is richer in electrolyte.

This view of the black lamella is further forced upon one by the fact that it passes almost abruptly into the coloured film. Gibbs [3] pointed out, and Reinold and Rücker [4] found, that the black spots are never bounded by a grey of the first order, that is, by thicknesses of 20 to 40 $\mu\mu$; the smallest neighbouring thickness observed was a white of the first order, about 100 $\mu\mu$ therefore. More frequently colours of higher order (above 300 $\mu\mu$) were found, so that sometimes the neighbouring part was over 100 times thicker than the black spot. This abrupt transition disappears when an electric current is sent through the lamella,[5] the path of the current being in the lamella surface, in such a way that the current passes from the thicker to the thinner part of the lamella. In place of the sharp transition the missing grey colours of the first order appear. If the current be interrupted the original abrupt transition is restored in ten to fifteen seconds.

This behaviour may no doubt be explained as follows. As soon as the micellæ of the two surface films of the lamella have approached sufficiently closely, the force of attraction takes effect, as observed in coagulation (cf. p. 432), and which permits the preparation of a uniform gel. The two films force out the liquid between them on account of their attraction. The effect of the electric current depends upon electrosmosis.[6] In a short time the two films are not united to such an extent, that the liquid cannot, as in a capillary, be driven between them electrosmotically from the thicker part of the lamella. In agreement with this view, the liquid moves in the same direction as the current. For there is no doubt that the films are negatively charged with respect to the solution. One might expect that

[1] *Reinold* and *Rücker*, Phil. Trans. **184**, A, 505 (1893).

[2] *Loc. cit.* p. 794. *Gibbs* (Scientific Papers, Vol. I, p. 312) already expresses the same view.

[3] Scientific Papers, Vol. I, p. 365 ; *loc. cit.* p. 793.

[4] Proc. Roy. Soc. **26**, 334 (1877).

[5] *Reinold* and *Rücker*, Phil. Mag. (5), **19**, 94 (1885).

[6] *Wiedemann* [Elektricität, I, 1012 (1893)] also explains the phenomenon on the basis of electrosmosis, without however taking the surface films into account.

after some time, when the films have united more closely, this experiment would succeed less and less readily.

The black film also alters quite reversibly with temperature and pressure. Thus Johonnott[1] found that a black lamella prepared from a sodium oleate solution and having a thickness of 15 $\mu\mu$ became thicker at lower temperatures (up to about 40 $\mu\mu$), doubtless on account of swelling, and thinner at higher temperatures, reaching about 5 $\mu\mu$. This reversibility implies that lamellæ even as fine as this, and hence a foam the lamellæ of which have in part become as fine, are far more stable than the fragility of the lamellæ would lead one to expect. That the black lamella is stable at all depends upon the fact that it is tough like a jelly and probably composed of long-fibred micellæ.

As regards surface tension, the black spots do not differ apparently from the coloured lamellæ.[2] If this were the case, indeed, rapid motion would have to take place on the lamellæ. The equality of the surface tension is intelligible when we consider that the black spot is bounded towards the gas space by the same surface layer as the coloured. The same cause accounts for the invariability of the surface tension over a large range of high concentrations in solutions of capillary-active substances (see p. 317).

This does not exhaust the various phenomena connected with the thickness of soap films. Newton mentioned two different kinds of black spots, and Reinold and Rücker,[3] Johonnott,[4] and Rickenbacher,[5] actually found that with many lamellæ the first black film is followed by a second as the thickness decreases. It appears to form suddenly, to be separated by a fairly irregular black line from the first film, and it is perhaps somewhat different from the first in surface tension, as according to Johonnott spots of the second black move around upon the spots of the first, although direct measurement does not show any distinct difference in surface tension. Rickenbacher found the electrically measured thickness of the second film to be about one-half that of the first—7·3 $\mu\mu$ against 13·5 $\mu\mu$; and similar results follow from Johonnott's[6] measurements. One might believe that the second black, in contrast to the first, consists of a single surface film.

The view here upheld, that black spots and coloured films are chemically different in so far as the black spot consists only of surface films, is less forced than a purely physical theory given by Reinold and Rücker.[7] They discuss the possibility that it is a matter of a phenomenon which is connected with the dependence of the surface tension upon the thickness of the lamella—corresponding to its dependence upon the size of particles (see p. 45); they suppose that the surface tension might even be smaller at thicknesses of 20 to 100 $\mu\mu$ than at the thicker parts, while for reasons difficult to understand it should again increase at the still smaller thickness of the black spots. Thus the black film might be in equilibrium with the coloured one at the same surface tension, but not with lamellæ of intermediate thickness. Up to the present no phenomenon is known, in which colloidal particles are unstable, when of a certain order of magnitude.

[1] *loc. cit.* p. 313.
[2] *Reinold* and *Rücker*, Phil. Trans. **177**, 627 (1886).
[3] Phil. Trans. **184**, A, 512 (1893).
[4] Phil. Mag. (5), **47**, 506 (1899).
[5] Kolloidchem. Beihefte **8**, 163 *et seq.* (1916).
[6] Phil. Mag. (6), **11**, 746 (1906).
[7] Phil. Trans. **177**, 679 *et seq.* (1886).

How the lamellæ arrange themselves in equilibrium to bubbles, and bubbles to foam, is entirely decided by the surface tension, which always strives for a minimum surface. It appears that never more than three lamellæ meet in an edge, and that never more than four edges or six lamellæ cut at a point, the lamellæ cutting one another at angles of less than 120°.[1] Bubbles of foam are therefore in section irregular hexagons with equal angles of 120°. If bubbles have been formed by blowing a foam in which more than three lamellæ meet at one point, the lamellæ slide over one another until the condition of equilibrium is fulfilled. This phenomenon may be readily followed in a large observation trough, the glass walls of which are distant about 1·5 cm. from one another, and in which some soap solution is blown into a foam.[2]

In such experiments the difference between the elastic lamellæ of soap and the rigid lamellæ of saponin becomes evident. With soap foam this rearrangement takes place with continual change in the thickness of the lamellæ and hence of the colour in such a way that one cannot follow with certainty the history of a single lamella. It is otherwise with saponin foam. The lamellæ are so rigid that certain spots of colour are preserved unaltered upon a lamella, and when in the striving after equilibrium certain lamellæ burst, or unite to form new ones, the history of the lamellæ in question can be read off on these invariable spots of colour.[3]

Since a single foam-bubble strives to become smaller on account of the surface tension, the gas in it is under pressure, which is the greater the smaller the radius of curvature of the bubble. Many experiments are known which make this pressure visible ; if a soap bubble is blown at the end of a tube, and then allowed to contract, the air emitted from the other end will blow out a candle. Hence a foam collects the air blown into it like an air cushion and is, like this, elastic and resistant to pressure. A second circumstance that makes a foam so resistant to the action of solid bodies is the following. If the solid body be wetted, as is the rule with readily wetting solutions such as those of soap and saponin, it is necessarily drawn into the canals rich in liquid at the corners of the bubbles, and need not disturb the structure at more distant points. Rhumbler[4] has made surprising experiments of this kind. Iron filings or lead shot can fall through a soap foam without changing the arrangements of the foam cells in any way. Mantles of foam, such as are frequently used by living organisms to envelop themselves, many therefore lend considerable protection.

The soap solutions required for the experiments discussed must be prepared with particular care. Plateau[5] recommends the following method. One part of Marseilles soap is dissolved at a gentle heat in 40 parts of distilled water and filtered ; 3 volumes of this solution are mixed with 2·2 volumes of glycerine. The mixture remains standing for 7 days, is then cooled to +3° by dipping into ice-water, and the resulting precipitate filtered at the same temperature. The filtrate is ready for use in a few days. Boys considers some changes in these directions as useful. He takes instead of Marseilles soap sodium oleate with distilled water in the above proposition, fills a flask three-quarters full with this solution, and fills up with glycerine after standing for one day. The mixture is then well shaken, allowed to stand in the dark for a week, siphoned off from the foam, and to each litre of liquid 2 to 3 drops of concentrated ammonia are added. The finished solution is preserved in the dark

[1] *Plateau*, "Statique des Liquides," I, p. 294 *et seq.*
[2] *Boys*, "Soap Bubbles," p. 120.
[3] *Boys*, "Seifenblasen," p. 84.
[4] Ergebn. d. Physiol. **14**, 526–7 (1914).
[5] "Statique des Liquides," I, p. 163.

in a stoppered bottle. Boys systematically avoids all warming and all filtration, and the admission of air to the liquid when keeping it.[1]

Ferric acetate solution may be mentioned as a solution of a more inorganic substance, which froths sensibly.[2]

D. DISPERSE STRUCTURES WITH SOLID DISPERSION MEDIA

Disperse structures with solid dispersion media are extremely widespread and important. Their detailed investigation proves to be very difficult. The ultramicroscope has led us farthest, but up to the present it could not be made use of quite generally, partly on account of the mechanical properties of the disperse structures and partly on account of their strong adsorption of light. An ultramicroscopic method applicable to extremely thin films of solids would be of great value. A further difficulty lies in the fact that all processes such as coagulation, peptization, as well as electrokinetic phenomena, are abolished more or less completely on account of the rigidity of the dispersion medium, and hence we must forgo the conclusions which could otherwise be drawn from them.

Solid Foams

Structures in which a gas is distributed in a solid skeleton have already been considered several times, for instance xerogels, and also the solid precipitates thrown down in gases (see p. 787). In their case we must regard it as certain that the gas does not actually form the disperse phase, but that the capillary spaces filled by it are connected together to a large extent. A true solid foam is obtained when an ordinary liquid foam solidifies on drying, as may happen, for example, with saponin foam.

That bubbles of glass may be blown is, as Boys[3] emphasizes, due to reasons quite different from those in the case of the production of soap bubbles. Glass has no tough surface films; when fused, on the contrary, it is perfectly homogeneous. But it is very tough and passes quite continuously upon cooling from the liquid into the solid state. In blowing glass the thinnest points become solid more quickly on account of more rapid cooling, the thicker ones are still soft and allow of further expansion to a uniform film. Upon the same reasons depends no doubt the fact that bubbles may be blown of molten resin to which some wax or paraffin wax has been added.

Solid Sols

Structures will be described as solid sols the dispersion medium of which is solid—crystalline or amorphous—while the disperse phase may be liquid or solid. We may also distinguish, when necessary, solid emulsoids and solid dispersoids.

A beautiful case of a solid emulsoid was observed by Gernez[4] with so-called black phosphorus. Thénard[5] had already described a preparation

[1] "Soap Bubbles," p. 142.

[2] *Plateau*, "Statique des Liquides," II, p. 20.

[3] "Seifenblasen," p. 81. See e.g. concerning the formation of pumice *Endell*, Zentralbl. f. Mineral. Geol. u. Paläont. 1915, p. 69.

[4] Ann. d. chim. et d. phys. (8), **21**, 1 (1910). This "black phosphorus" is entirely different from the black phosphorus obtained by *Bridgman* by the action of high pressures upon phosphorus [Journ. Amer. Chem. Soc. **36**, 1344 (1914)].

[5] Ann. d. chim. **81**, 109 (1812).

of phosphorus which became black on solidification; he obtained it by chance, but was unable to prepare it again. Blondlot [1] at first met with similar difficulties, until he succeeded in proving that the phosphorus must be heated with mercury in order to obtain the black phosphorus; it is dyed, as it were, by the mercury. Gernez was able to explain the phenomenon completely; mercury dissolves somewhat in molten phosphorus, this dissolution taking place particularly easily when the surface is large, as is the case if the phosphorus be allowed to react with a mercury salt. The mercury is dissolved in a colourless form in molten phosphorus. If rapid cooling takes place it separates upon solidification in innumerable ultramicroscopic globules, which permeate the phosphorus uniformly and colour it black. The globules could actually be recognized in the ultramicroscope. Their properties entirely agreed with those of metallic mercury.

Numerous examples are known in which one solid substance is distributed in a state of fine division throughout a second. Many glasses, such as the well-known gold ruby glass, belong to this category and are to be counted among the oldest colloidal substances made technically; further the photohalides frequently mentioned, and among naturally occurring structures blue rock salt, etc. Before we deal with these in detail, it may be mentioned that Gernez [2] prepared a number of such solid sols in connexion with his experiments mentioned above. Thus mercuric iodide dissolves in molten phosphorus, and also in organic substances such as paraffin, naphthalene, salol, thymol, benzophenone, and many others, and separates upon solidification in an extremely finely divided form, at first in the yellow form, which is unstable below 126°. This changes in course of time more or less quickly into the red form stable at room temperature.

Ruby Glasses

Gold ruby glass is not only one of the oldest technical colloidal products, but also the first substance upon which the nature of the colloidal state was elucidated by aid of the ultramicroscope.[3] This investigation succeeds well with the slit ultramicroscope, if in place of the observation trough a parallelopiped of gold ruby glass is introduced, the surface of which towards the illumination objective is highly polished. The careful polishing of the surface is necessary, since otherwise a sharp image of the slit is not formed in the interior of the glass. The necessity for giving the solids investigated a polished surface is one of the difficulties of their ultramicroscopic investigation. With a suitable gold content of the glass the ultramicroscopic picture is exactly like that of a gold sol, except that the particles are at rest.

A ruby glass of this kind is best obtained when gold is added to the molten glass either in the form of purple of Cassius, as used by Kunkel, the discoverer of this glass, or in the form of some gold salt or other; the melt is then rapidly cooled and reheated. The quickly cooled melt is colourless. In what form the gold is contained in it does not appear to me to be definitely settled. Zsigmondy [4] holds the view that it is not chemically combined, but present in true supersaturated solution. In favour

[1] Compt. rend. **60,** 830 (1865); **70,** 856 (1870); **78,** 1130 (1874). Ann. d. chim. et d. phys. (8) **21,** 283 (1910).

[2] *Siedentopf* and *Zsigmondy, loc. cit.* p. 2.

[4] "Zur Erkenntnis der Kolloide," Jena, 1905, p. 128 *et seq.* "Kolloidchemie," 3rd ed., p. 36.

of this view he points out in the first place that the melt is at first colourless even in the presence of strong reducing agents; further, that the whole behaviour may be readily explained on the basis of the well-known properties of the velocities of the formation of nuclei and of crystallization. The nuclei arise from a supersaturated solution upon cooling, and grow upon warming on account of the increased crystallization velocity. Against this view it may be urged that other experimental results lead us to expect that a true solution of gold would not be colourless, but would have the colour of gold vapour (cf. p. 386), and that colloidal solutions of the alkali metals actually show the colour of the metallic vapour in question. It has already been pointed out, on the other hand, that this is not necessarily the case, and that metals collected in a suitable salt layer when cathodically disintegrated, and dispersed atomically in it, do not colour it (see p. 788).[1] If it were a matter of a gold compound, the gold would separate on warming in a finely divided form. That rays of radioactive substances are also able, in place of heating,[2] to produce the red colour in the colourless glass does not necessarily mean a destruction of the chemical compound, but might also imply the abolition of a labile state of solution. The fact that the coloration produced by the radiation is uniform throughout the glass points to the β-rays being the active cause.[3]

If the colourless glass is warmed too strongly or too long, the glass is coloured blue and brown, the gold particles coagulate, become coarser in the glass when sufficiently limpid, and the colour changes appear which were described on p. 383. In accordance with the great colouring power of colloidally dissolved substances, a very small amount of gold, 0·1 g. to 1 kilo., is sufficient to give the glass a strong red colour.[4]

Other ruby glasses, such as those of silver, copper, selenium, etc., behave similarly to gold glass. In the case of copper ruby glass, glasses with particles of quite different sizes are made use of technically: the true ruby glass with ultramicroscopic particles, the opaque copper-red hæmatinon with microscopically visible particles, and Aventurine glass containing copper particles visible to the naked eye.[5] These glasses also behave towards radium rays as does gold glass.[6]

As regards the state of aggregation of the metals and the shape of their particles, the same is true as was remarked on p. 413. They are probably crystalline, but depart very little from the spherical form, as the red colour of ruby glass teaches us.

A similar substance to these glasses is a slag containing manganese in highly disperse form described by R. Lorenz.[7]

A number of probable reasons exist for assuming that colorations produced by sulphur, for instance in *ultramarine*, and even in organic sulphur dyes, depend upon a colloidally disperse distribution of the sulphur (or of certain sulphur compounds).[8] The following are the chief reasons. The

[1] *v. Weimarn* [Kolloidzeitschr. **11**, 287 (1912)] points out that in natural gold-bearing quartz the gold may also appear in colourless dispersion.

[2] According to *Soddy*, quoted from *Maxwell Garnett*, Phil. Trans. **203**, A, 400 (1904).

[3] *Maxwell Garnett*, Phil. Trans. 205, A, 267 (1906).

[4] See *Keppeler* in *Dralle*, "Die Glasfabrikation," München and Berlin, 1911, p. 128.

[5] *Keppeler* in *Dralle*, "Die Glasfabrikation," p. 130.

[6] *Maxwell Garnett*, Phil. Trans. **205**, A, 259 *et seq.* (1906).

[7] Zeitschr. f. anorg. Chemie, **92**, 35 (1915).

[8] *W. Biltz*, Nachr. Ges. Wiss. Göttingen, 1904, p. 307; *Wo. Ostwald*, Kolloidchem. Beihefte **2**, 449 *et seq.* (1911); Kolloidzeitschr. **12**, 61 (1913); "Die Welt der vernachlässigten Dimensionen," p. 154.

colours are very diverse and dependent upon small changes in the composition of the reacting substances ; with ultramarine the mixture of sulphur, silicates, and salts is melted together at a high temperature and the grey or yellowish "mother of ultramarine," just as with gold ruby glass, is only transformed into ultramarine by renewed cautious heating ; blue sols may also be obtained in other dispersion media (molten borax, glycerine) which may be regarded as sols of sulphur. The ultramicroscopic detection of disperse sulphur has not yet been successful.

Coloured Salts

Colloidally disperse structures which belong to this class have already been described (p. 657) in the case of the crystals formed upon solidification of Lorenz's pyrosols :—lead chloride crystals containing colloidally dispersed lead, thallous chloride with thallium as disperse phase, and so on. Although turbid, these crystals were sufficiently transparent, and surfaces of sufficient smoothness could be produced in them to permit of the elucidation of their structure by means of the ultramicroscope. They are formed even by cooling the molten salts in question ; and in a very marked form when the molten salt is allowed to act upon the metal in question, or is reduced.

As prototypes of such coloured salts we might take the coloured alkali halides, coloured rock salt, such as occurs in nature, and the coloured crystals of sodium chloride, potassium chloride, and others, which may be prepared artificially in various ways. All these methods depend in some way upon attempting to bring alkali metal in a highly disperse form into the crystal. For this purpose either the vapour of the metal is allowed to act upon the carefully dried crystal at temperatures 50° to 80° lower than the boiling-point of the metal (at lower temperatures the vapour pressure is too small, at higher ones the metal evaporates again from the salt), or the salt is irradiated with ultraviolet light, X-rays, cathode rays, the rays from radioactive substances, and so on, under the influence of which a decomposition of the salt with production of the free metal is possible. Naturally occurring coloured rock salt is generally blue, but other colours such as violet, and then greenish, red, or yellow, occur.[1] The artificially coloured salts are usually yellow, brown, or green. On heating they become blue, violet red, yellowish, and finally colourless.

Siedentopf [2] has shown that in all these coloured salts—with the exception of those coloured quite a light yellow—ultramicroscopic particles, which have completely the character of metallic particles, such as are present in metal sols or ruby glasses, may be recognized. They are strongly coloured, usually reddish or brownish, but other colours also appear—yellow, green, blue—so that the ultramicroscopic picture of these crystals is one of the most beautiful. As required by the Tyndall phenomenon, the colour as seen in the ultramicroscope is complementary to that of the transmitted light of the majority of the particles. The artificially coloured salts show this difference of colour quite distinctly even with macroscopic observation. This is not perceptible with the natural blue rock salt, since the micella content is too low. Not only does the appearance of these

[1] *Kreutz*, Abh. d. Akad. d. Wiss. z. Krak. 1892, p. 147 ; 1895, p. 118 ; 1896, p. 112.

[2] Verh. d. deutsch. physik. Ges. **7**, 268 (1905) ; Physik. Zeitschr. **6**, 855 (1905). Concerning the possibility that natural blue rock salt differs from artificial, see *Spezia*, [Zentralbl. f. Mineral. u. Geol. 1909, p. 398].

micellæ and the method of preparation of the coloured salt favour the view that the particles consist of the metal ; but it may further be adduced as proof that the colour disappears at the boiling-point of the metal. In the arrangement of the particles it is worthy of note that not only does an irregular, cloudy distribution occur, but also one of rows fairly uniformly arranged and cutting one another. This is to be interpreted as due to the presence in the crystal of cleavages, in which the particles are preferentially deposited.

The polarization of the Tyndall beam does not correspond to the case in which all the particles are spherical. This is recognized when one employs polarized light with the direction of vibration parallel to the direction of observation. Then the particles should be invisible in the ultramicroscope (see p. 380). Actually, however, only those irregularly arranged disappear. The others remain recognizable, and send out light polarized in various directions, as may be recognized by turning the analyser. The particles are further found to be pleochroic. This all favours the view that the particles are not all spherical, but disc- or rod-shaped, and it is further probable that they take this form under the influence of external pressure.

For Siedentopf [1] was able to show that the micellæ of blue rock salt become markedly dichroic when the crystals are pressed. If we assume that under the pressure metallic spheres are transformed into discs, the observations may be represented as follows. If the direction of pressure is at right-angles to the direction of observation, if therefore the direction of observation lies in the plane of the disc, then the light scattered sideways, by which these particles are seen in the ultramicroscope, will be orange-brown or green. It is orange-brown when the direction of vibration of the incident polarized light lies in the plane of the disc ; green, when it is at right-angles to the disc. The light of shorter wave-lengths is sent out when the direction of vibration is parallel to the short axis of the disc-shaped ellipsoid ; the light of longer wave-length when it lies parallel to a long axis of the ellipsoid. If the direction of pressure is parallel to the direction of observation, if therefore the direction of observation is at right-angles to the surface of the disc, the particles are only orange-brown

TABLE 192

Dichroism of Coloured Rock Salt under Pressure

Direction of Pressure.[2]	Direction of Vibration.	Direction of Observation.	Colour of Diffraction Discs.	Colour of Transmitted Light.
—	—	.	Green	Red
—	|	.	Orange-brown	Blue
|	—	.	Orange-brown	Blue
|	|	.	Green	Red
.	—	.	Orange-brown	Blue
.	|	.	Orange-brown	Blue

[1] Verh. d. deutsch. physik. Ges. **9**, 621 (1907) ; **12**, 6 (1910).
[2] — means from right to left or vice versa.
| „ „ above to below or vice versa.
. „ „ front to back or vice versa.

For one only receives light vibrating in the plane of the disc, none vibrating at right-angles to it. The transmitted light is always complementary: blue, when the particles appear orange-brown in the ultramicroscope; red, when they are green. Table 192 gives a general view of this behaviour.

In course of time, more quickly on warming, the dichroism disappears again.

As far as I can see, this behaviour agrees with the theory developed by Gans (p. 385), in so far as Tyndall light of longer wave-length is preferentially produced, when the direction of vibration is parallel to the direction in which the particle is more extended.

The Photohalides

The photohalides already frequently mentioned belong to the class of coloured salts (see p. 658). They are silver halides containing silver micellæ and are formed under very diverse conditions. They may be prepared by incomplete reduction of silver halide; thus Carey Lea [1] was the first to prepare photochloride by chemical means, by reducing silver nitrate or ammoniacal silver oxide with ferrous oxalate or pyrogallol. Or conversely, a halogen may act upon silver without complete oxidation occurring. Baur,[2] for instance, obtained sols of photochloride by treating silver sols with an amount of chlorine water insufficient for complete chlorination. The most conclusive information concerning the nature of these substances is given by the methods of preparation in which silver is allowed to act directly upon silver halide. Carey Lea [3] was the first to effect this successfully by boiling freshly precipitated silver chloride with finely powdered silver, and precipitating from the suspension a red photochloride. R. Lorenz [4] prepared it by allowing silver to act upon molten silver chloride at 1,100°; Günther [5] by causing colloidal silver to act upon flakes of silver chloride; and Reinders,[6] by crystallizing silver chloride from an ammoniacal solution containing colloidal silver.

Since silver compounds are readily reduced to silver by light, it is natural that the photohalides are produced particularly by illumination of silver halide; this fact led Carey Lea to term them photohalides. Silver halide coloured by light simply consists of the photohalide.

They show to a large extent the properties which one might expect from the behaviour of metal sols, coloured salts, and so on: in the first place very diverse colours—yellow, reddish, blue, violet—the trustworthy explanation of which would require a knowledge of the size and shape of the silver micellæ in each individual case. They further show strong colouring power in very small concentrations. R. Lorenz [7] was able to detect ultramicroscopically the presence of submicrons in the AgCl crystals containing silver. For a long time one hesitated to regard the colour-producing substance in the photohalides as metallic silver, since it is dis-

[1] "Colloidal Silver and the Photohalides."

[2] Zeitschr. f. physik. Chemie, **45**, 613 (1903).

[3] "Colloidal Silver and the Photohalides."

[4] Zeitschr. f. Elektrochemie, **7**, 281 (1900); "Die Elektrolyse geschmolzener Salze," **2**, p. 64, Halle, 1905; *R. Lorenz* and *Eitel*, Zeitschr. f. anorg. Chemie, **91**, 57 (1915).

[5] Abhandl. d. naturhist. Ges. Nürnberg, **15**, 26 (1904); see also *Lüppo-Cramer*, "Kolloidchemie und Photographie," 2nd Ed., Dresden, 1921; p. 25 *et seq.*

[6] Zeitschr. f. physik. Chemie, **77**, 213 (1911).

[7] *R. Lorenz* and *Eitel, loc. cit.* under [4].

solved out by nitric acid with such difficulty, and hence it was assumed that sub-halides of silver are formed, of which, on account of the variety of colours, the existence of a whole series had to be assumed. That this objection does not hold good was shown by Lüppo-Cramer.[1] Whether the colloidal mixture of silver and silver halide is attacked by nitric acid, chromic acid, and so on, depends essentially upon the size of the particles; if they are fine, the silver is dissolved out; if coarse, this takes place extremely slowly or practically not at all. Lüppo-Cramer[2] was able to prepare in the manner above described photo-bromide mixtures from Ag and AgBr sols, from which nitric acid would not remove the silver after coagulation. The silver is therefore protected by the silver halide in which it is embedded, a behaviour frequently observed in colloidal mixtures. Mercury is unable to dissolve the gold from purple of Cassius, since it is protected by stannic acid[3]; Zsigmondy[4] mentions that stannic acid, as protective colloid, will protect oxides such as copper oxide from dissolution by nitric acid.

Upon the basis of the knowledge that silver halide coloured by light is silver halide containing silver micellæ, the nature of the latent image was successfully explained. R. Lorenz[5] was the first to suggest that the substance of which the latent image consists is none other than a photohalide, in which the silver micellæ first separated are present in such small amount that they cannot be recognized by the colour, but are able to serve as nuclei during the further reduction of silver halide. In favour of this view we have the fact that upon illuminating optically empty silver chloride crystals the micellæ are at once recognizable, a process which is then carried on until photochloride recognizable by its external characteristics is produced.[6] No less demonstrative is the following experiment by Siedentopf.[7] When a silver chloride sol is examined under the paraboloid ultramicroscope, alongside the whitish AgCl micellæ coloured particles immediately appear, which we are fully justified in regarding as silver micellæ. Lüppo-Cramer[8] has systematically followed up the idea that the latent image consists of photohalide, and elucidated to a great extent the phenomena occurring in photographic processes.

A curious property of photochloride consists in the fact that when illuminated by coloured light, it assumes to a large extent the colour of the incident light, and hence allows of colour photography to a certain extent.[9] The colours red and blue, in particular, are correctly reproduced. This phenomenon already discovered by Seebeck[10] is probably connected with the changes, to be discussed later (p. 810), of the photohalides in light, which were discovered by Weigert.

[1] Photographische Probleme," Halle, 1907, p. 62 *et seq.*
[2] "Kolloidchemie und Photographie," 2nd Ed., Dresden, 1921, p. 26.
[3] *Zsigmondy*, Lieb. Ann. **301**, 378 (1898).
[4] "Kolloidchemie," 3rd Ed., p. 297.
[5] *loc. cit.* p. 803.
[6] *R. Lorenz* and *Hiege*, Zeitschr. f. anorg. Chemie, **92**, 27 (1915).
[7] *loc. cit.* p. 488.
[8] Especially in "Photographische Probleme," Halle, 1907; "Kolloidchemie and Photographie," 2nd Ed., Dresden, 1921; "Das latente Bild," Halle, 1911, and a large number of papers in Kolloidzeitschr., Vols. **1** to **21**, **23** to **24**, **28**.
[9] See *Eder*, "Handbuch der Photographie," I, 3, p. 287 *et seq.*, Halle, 1912.
[10] *Eder*, "Handbuch der Photographie," I, 1, p. 118, Halle, 1905.

Colloidally Disperse Structures in Metallurgy

It has been pointed out on various sides,[1] with justice, that in the metallurgy of alloys the existence only of true solutions of the components in question or of coarsely disperse systems has been assumed, but that no good reason can be seen why colloidally dispersed structures should not frequently exist. It is difficult, no doubt, to characterize them, since, as is obvious, almost all our usual methods for proving the existence of the colloidal state fail us.[2] Nevertheless Benedicks already came to the conclusion that among the structural constituents of iron-carbon alloys troostite is to be regarded as a colloidal solution of cementite in ferrite. He drew this conclusion from the following data. Many transitions may be distinguished between structural components which appear upon rapid cooling of the molten metal, such as martensite, which one will regard as in true solution, and coarse lamellary components, such as pearlite, which appears on slow cooling. The assumption now readily suggests itself that a component, such as troostite, which appears under intermediate conditions, is also intermediate in its properties, and hence finely disperse.

Colloidally Disperse Structures with more than Two Phases

In the theory of the photographic plate we already meet with a circumstance of importance for the further development of colloid chemistry. It is not a simple matter of the photohalides, that is, a two-phase system of silver halide and silver, but this system is embedded dispersely in a gelatine layer which itself consists of two phases ; and between the four phases, the two of the photohalide, the gelatine micellæ, and water (or aqueous solution) we have very lively and manifold interaction. Similar structures have been discussed earlier, for instance in connexion with Liesegang's rings (see p. 732), where the strong influence of the nature of the gel also appeared. Foams also belong, strictly speaking, to this section, for when they are durable we have doubtless always to reckon with a solid phase contained in the gel layers coating the lamellæ, and not only with liquid and gaseous phases. It is at present still difficult to set up general rules for the behaviour of these polyphasic structures, although some optical properties in particular have been to a large extent elucidated.

In the first place we have the phenomena which have been observed in gelatine gels containing gold or silver micellæ. Such gels are obtained by allowing a gold or silver sol mixed with gelatine to dry. The colour of such jellies depends greatly, as Kirchner and Zsigmondy[3] showed, upon their water-content. If for instance a highly-dried, extremely thin gelatine gel containing gold is blue or violet by transmitted light, and lustrous brown by reflected light, it becomes, on moistening, red by transmitted and green by reflected light ; upon renewed drying the gel again becomes

[1] *Benedicks*, Zeitschr. f. physik. Chemie, **52,** 6 (1905) ; Kolloidzeitschr. **7,** 290 (1910) ; *Wo. Ostwald*, "Die Welt der vernachlässigten Dimensionen," Dresden and Leipzig, 1915, p. 163 *et seq.* Kolloidzeitschr. **19,** 46 (1916) ; *Wa. Ostwald, ibid.* **26,** 138 (1920).

[2] *Wa. Ostwald* (*loc. cit.* under [1]) wishes to draw conclusions concerning the states of colloidal or true solution from liquation phenomena : with a true solution, the dissolved substance collects in the mother liquor, with colloidal solutions it is uniformly distributed in the solid. The conclusion would be more convincing if with these alloys a strong tendency to form solid solutions did not exist. [See also *Arnold* and *W. Sander*, Zeitschr. f. Metallkunde, **13,** 122 (1921).]

[3] Ann. d. Physik (**4**), **15,** 573 (1904).

blue, and this experiment can be frequently repeated. Kirchner [1] found similar phenomena with developed silver bromide gelatine plates. The oldest observations of this kind go back to Faraday.[2]

The phenomenon may be explained as follows, as shown by Kirchner and Zsigmondy. In a dried gel the gold particles have associated to coarser lumps or flakes. These flakes can actually be seen with the strongest magnifications of the microscope, while in the original sol the gold micellæ were only recognizable ultramicroscopically. When the gelatine gel loses water, the gold particles are therefore collected together locally. As has frequently been emphasized in other connexions (see p. 454), they do not then coalesce, indeed hardly touch one another, but remain separated by ultramicroscopic films of gelatine. Nevertheless the particles are so close to one another that the flakes affect the light as a whole, and hence according to Mie's theory give brown Tyndall light and are blue by transmitted light. If the gelatine films are allowed to imbibe moisture, the gold micellæ are forced so far apart that they again affect the light singly, and in accordance with their size scatter green light, and appear red by transmitted light. This experiment may be regarded as a proof that the association of colloid particles is fundamentally reversible, even in pure aqueous sols ; but processes taking place later appear to be responsible for the fact that flocculation assumes an irreversible character.

It further appears from these experiments that as in the case of sols, in gels also the micellæ associate to larger flakes, but it remains an open question whether, as in the case discussed, the micellæ always remain separated by films, or whether they also coalesce more completely. If the latter is correct, it remains to be decided whether the flakes are formed directly on account of the association of the micellæ, or whether, on account of the increase of solubility with decrease in the radius of curvature (see p. 155), the smallest particles have dissolved, while the originally coarser particles have grown. This process takes place perhaps in the ripening of silver bromide gelatine emulsion, in which the originally very fine particles of silver bromide are allowed to become coarser, because plates made with such coarser particles are more sensitive. It might appear surprising that plates with coarser particles are more sensitive. According to Liesegang [3] it is not in this case necessarily a matter of a greater sensitiveness to light, but of a greater sensitiveness upon development, and this would be intelligible. With very small silver bromide micellæ it is highly probable that the particles are transformed into silver as a whole, or that the silver particles do not remain invariably bound to bromide, but on account of the disintegrating effect of light mentioned above, are thrown out of the micellæ. This is unfavourable to chemical development, since it can take place more quickly the nearer the silver nuclei lie to silver bromide. If the silver bromide particles are larger the probability of silver particles remaining attached to them is greater ; indeed, almost always to be expected. Perhaps the circumstance mentioned on p. 235, that a certain size of micella is necessary in order that they may act as adsorbents, also plays a part.

A further group of phenomena is related to the sensitiveness to pressure considered above (p. 802), of sodium micellæ contained in rock salt. Herm.

[1] Ber. Sächs. Ges. d. Wiss. z. Leipzig, math.-phys. Kl. **54,** 261 (1902).
[2] Phil. Trans. **147,** 157 (1857).
[3] "Photographische Chemie," Düsseldorf, 1898, p. 110.

Ambronn has shown how a dichroism may be produced by mechanical action in many gels containing micellæ.[1] The experiment performed by him, which may perhaps be regarded as the fundamental experiment in connexion with all these phenomena, was as follows. In the very narrow black spaces which are formed when the carefully cleaned surfaces of a cover-glass and microscope slide are pressed together, he produced crystals of silver or gold by reduction (the former, for instance, by illuminating a solution of $AgNO_3$). Very fine silver films were formed which were united to nodules or sometimes to sphæro-crystals. All were distinctly pleochroic in polarized light, the leaflets indigo blue to yellow, or also light blue to red-violet, the sphæro-crystals only indigo blue and yellow ; with these, therefore, two blue and two yellow sectors were present, the direction of vibration of the polarized light passing through the blue sectors. With gold, needle-shaped crystals were produced with pleochroism from wine red to blue green. As before (p. 410), the question again arises, whether the pleochroism is due to the anisotropic arrangement of isotropic structural units, or whether the structural units themselves are anisotropic. Herm. Ambronn leans to the second view, since the crystals thus formed appear to be labile and have a form different from that of the ordinary regular crystals. He interprets the two kinds of pleochroism occurring with silver as indicating that the crystals formed are optically binaxial. He also points out that the crystals in themselves have a labile character, for if the cover-glass is removed, the silver plates are transformed into a metallic shining mirror, whereby the external outline changes, and the colour by transmitted light changes from dark grey blue to deep steel blue. But since it has been shown that the finest particles of gold and silver sols have the same crystalline structure as larger crystals (see p. 413), I should prefer to regard it as more probable that in these experiments also smallest particles of the ordinary crystal form occur, but that in the narrow space they are forced into entirely irregular and hence unstable forms of growth. The two different kinds of pleochroism observed with silver are perhaps connected with the same circumstances which produce red and yellow sols with extremely fine silver particles.

Gold and silver micellæ in mechanically stressed gels behave very similarly. Thus Herm. Ambronn and Zsigmondy [2] allowed gelatine gels containing gold and silver, such as may be obtained by mixing gelatine solution with gold and silver sols, to swell, stretched them, and allowed them to dry under tension. The gels were dichroic, that of gold being red by transmitted light when the direction of vibration of the incident light was at right-angles to the direction of extension ; blue-violet when the two directions were parallel. A quite similar dichroism was observed by Ambronn [3] when naturally occurring anisotropic structures, such as wood

[1] Zeitschr. f. wiss. Mikroskopie, **22,** 349 (1905). Connected with this dichroism is probably the dichroism and double refraction of metallic mirrors prepared according to *Kundt's* method [Wied. Ann. **27,** 59 (1886)] by cathodic disintegration. It cannot be a double refraction due to mechanical strain, according to *Rumpelt* ["Über Doppelbrechung in Metallschichten," Diss., Leipzig, 1908], but rather a rod double refraction. Perhaps the electrical properties of the metallic particles or the conditions of their impact upon the glass cause similar changes in their growth and arrangement as in the formation of layers of metal in narrow spaces. [H. *Ambronn*, Physik. Zeitschr. **8,** 665 (1907).]

[2] Ber. math.-physik. Kl. d. Sächs. Ges. d. Wiss. z. Leipzig, **51,** 13 (1899).

[3] Ber. d. math.-physik. Kl. d. Sächs. Ges. d. Wiss. z. Leipzig, **48,** 613 (1896); further, *E. Kolbe*, "Über die Färbung von Pflanzenfasern mit Silber und Goldsalzen," Diss., Jena, 1912.

fibre and hair, were soaked in solutions of gold and silver salts. The metallic salts were thereby reduced, and dichroic gold or silver suspensions were produced. From the formation of labile pleochroic crystals in narrow capillary spaces, above described, it is only plausible to assume that these crystals also separate in the capillaries of the gel, and are then similarly orientated by the mechanical stress, in the case of gelatine, or by the natural structure of the gel as in the case of fibres and the like, and thus cause the pleochroism of the gel. This quite corresponds to what we should expect; the colour of the transmitted light is of long wave-length when the direction of vibration of polarized light is at right-angles to the length of the particles, and hence at right-angles to the direction of extension; it is of short wave-length when the direction of vibration is parallel to the length of the particles and to the direction of extension (see Table 192, p. 802).

Now it is surprising that in many cases the light itself, in place of mechanical stress, can produce dichroism. These are the fundamental phenomena recently discovered by Weigert,[1] which are observed especially in connexion with layers of photochloride. If a printing-out paper which has turned brown in daylight, or a silver chloride collodion layer on a glass plate be illuminated by linearly polarized light, a red spot is produced. Seen through a Nicol this appears dichroic, being brightest when the direction of vibration of the electric vector of the light used for illumination agrees with that by means of which the spot is observed. The experiment succeeds with the colours from red to greenish blue, the effect decreases greatly with decrease in wave length, so that it is no longer recognizable in the blue and violet. It is important that the spatial displacement with which we have to reckon lies in the direction of the electrical vector of the exciting light. This is recognized by an experiment in which the direction of the exciting light is at right-angles to the direction of observation. The polarized light falls through the bottom of a narrow trough filled with the layer of photochloride, while the layer is examined at right-angles to the broad side of the trough. Dichroism appears when the electrical vector of the exciting light lies in the plane of the layer, not when it is at right-angles thereto.

Along with the dichroism, which may be designated *photodichroism*, double refraction arises. The spot produced by polarized light causes light to pass between crossed Nicols, indeed, the difference between polarized and unpolarized light can be rendered directly visible without the use of a Nicol. If a spot is produced by illuminating a silver chloride gelatine plate for a certain time with polarized red light, and if a second spot be illuminated for half the time with light of the same direction of vibration, while in the second half of the time the illumination takes place with light at right-angles thereto, the second spot is brighter than the first, especially when both are examined through a red filter.

Dichroism and double refraction are closely connected with the change in colour of photochlorides which leads to their assuming the colour of the incident light (see p. 804).

The same phenomena, dichroism and double refraction, may be observed with light-sensitive dyes, such as cyanine, pinacyanol, pina-

[1] Ber. d. deutsch. physik. Ges. **21,** 479, 615, 623 (1919); Zeitschr. f. Physik. **2,** 1 (1920); **3,** 437 (1920); **5,** 410 (1921); Ann. d. Physik, **63,** 681 (1920); Kolloidzeitschr. **28,** 115 (1921); *Weigert* and *Pohle, ibid.* **28,** 153 (1921).

chrome, orthochrome, and others, when they are illuminated by polarized light when dissolved in collodion layers.

For the theory of these processes the following facts must be especially noted. They are not confined to the case in which the photochloride micellæ are embedded in a rigid gel, but also appear when they are in a liquid emulsion. We have therefore to deal with changes in the micellæ themselves, and since the embedment of the particles in the gel is not essential, we might have dealt with these phenomena in the section under photohalides. It further appears probable from the ultramicroscopic investigation that it is not the submicrons that are mainly responsible for the phenomenon. This may be deduced from the fact that the assumption of the colour of the incident light, which is closely connected with the dichroism, cannot be recognized ultramicroscopically as a change in the colour of the submicrons. The submicrons of the photochloride originally present are colourless. The appearance described by Siedentopf of coloured micellæ from the colourless silver halide micellæ (p. 804) is also observed here with the photochloride micellæ only upon strong illumination by light of short wave-length ; in red light no change of colour can be observed, and in this light the assumption of colour and dichroism are most pronounced. Hence Weigert assumes that it is a matter of changes in the amicrons (see also p. 411). The silver ions do not cause the phenomenon ; it disappears when the metallic silver is changed to silver ions by chemical action. Along with the change in colour of the submicrons in light of short wave-length mentioned above, a disintegration no doubt takes place, as described by Siedentopf also for benzopurpurin micellæ. But this coarse mechanical action of the light must for the same reason, namely that it only occurs with light of short wave-length, be distinguished from the mechanical action which is responsible for the production of photodichroism.

Weigert arrives at a theory of these phenomena which agrees well with existing data, by transferring to the behaviour of the silver in the photochloride micellæ the theory of colour change by association of small metallic micellæ to larger groups, as is important in connexion with the investigations of Maxwell Garnett, Mie, and Kirchner and Zsigmondy (see p. 382). It is here immaterial whether we are dealing with single atoms of silver or with small silver micellæ. He applies the conception of the *optical packing density* ; it is characterized in the first instance as the volume of the metal contained in unit volume of the medium, the photochloride, in which it is embedded, and this conception should include all the influences exerted upon the light by the metallic particles on account of their size, arrangement, and so on. The greater the optical packing density, the further the absorption band lies in the region of the spectrum of long wave-length ; for the more closely the particles are packed, the more strongly do their electrical fields influence one another on account of the *Stark effect*. The exciting light is now supposed to alter the optical packing density in such a way as to diminish it in the direction of the electric vector ; the micella is extended, as it were, in this direction. Weigert further makes the assumption that in the original photochloride micellæ the optical packing density is not uniform, but largest in the centre and decreases towards the periphery.

It would lead us too far here to show how the extremely complicated dependence of photodichroism upon the colour of the exciting light and upon the duration of the illumination may be explained, according to Weigert, on the basis of the dependence determined by Maxwell Garnett of

the absorption constants in various spectral regions upon the optical packing density of the silver micellæ. As an example only the following will be sketched. Upon illumination with polarized red light the extension is greatest where the absorption is strongest, namely in the centre of the photochloride micella; for there the optical packing density is greatest. Hence it is there reduced in the direction of the electrical vector of the exciting light, and accordingly the absorption of red is decreased in the same direction; we have normal dichroism for red. For the other colours the photodichroism is quite different, it may even have the opposite sign. For by the decrease in the optical packing density the absorption for another colour of shorter wave-length may be increased; in the direction of the electrical vector we have an *increased*, and not a diminished, absorption of this colour. When the duration of the illumination is increased the optical packing density also alters in further regions not so near to the middle point, which absorb red more weakly, but still strongly enough. This change may lead to values of the packing density with which even a *diminished* absorption of the light of short wave-length takes place. One thus actually finds that after longer duration of the red illumination an initially negative dichroism for green becomes a positive one. It is also obvious why the rays of short wave-length, such as blue and violet, do not exert any influence. They are most strongly absorbed in the peripheral areas, in which the packing density is from the start so small that a change in it makes no difference.

The connexion with the assumption of incident colour also becomes intelligible. The originally dark photochloride absorbs all colours. If we illuminate with ordinary red light, only those regions are affected which absorb red in consequence of their optical packing density. Their packing density is thereby diminished in consequence of the extension assumed by Weigert, and hence likewise their power of absorbing red. Hence the photohalide now allows the red to pass. The same is true of any other colour.

Weigert [1] rightly points out that the assumption of colour so common in nature is almost certainly to be included in this group of phenomena.

Colloid chemistry thus ends to-day with a still very incomplete picture of phenomena in polyphasic structures, and it is precisely with these that the theory of many technical and biological phenomena must commence. The phenomena in photographic plates just referred to several times do not by any means stand alone. We have further to think of the many substances of technical importance, such as wood, fibres, starch, and so on, which are probably adsorption compounds of two or several colloids, or more correctly which contain two or several kinds of micellæ in addition to the imbibed water. In wood we have cellulose and lignin, in starch probably amylopectin and amylose; bread and many other foodstuffs have a similar character. In considering the process by which bread becomes stale, we have according to Katz [2] to take into account both the exchange of water between the very different micellæ of the crumb and the crust, and also changes produced in the starch micellæ of the crumb as regards their water content. At the present time there exists great difficulty, which is seldom overcome, in determining whether micellæ of different

[1] *Weigert*, Pflüg. Archiv, **190**, 177 (1921).

[2] Zeitschr. f. Elektrochem. **19**, 202, 663 (1913); Zeitschr. f. physiol. Chemie, **95**, 104, 136, 147 (1915); **96**, 314 (1916); *Verschaffelt* and Frl. *van Teutem*, *ibid.* **95**, 130 (1915).

kinds really are present alongside one another. Staining methods fail, when the micellæ are very intimately mixed with one another. If a possibility existed of examining ultramicroscopically such coloured polyphasic gels, great advance could probably be made. Perhaps it will be possible to make use of the peculiarities of the highly sensitive Liesegang rings and in general of the manner in which particles of a solid substance separate, to draw conclusions as to the presence and absence of the micellæ of a substance and their arrangement. Marriage,[1] at Hatschek's suggestion, successfully detected adulterations in jellies and like substances with the aid of these rings. We might also think of the possibility of attempting the separation of the micellæ of a very finely powdered gel, by a method similar to the flotation method, into those which, being hydrophobic, remain at the interface between two liquid phases, while the more hydrophilic enter the water. An extremely fine state of subdivision might perhaps be attained by means of the colloid mill (p. 474).

The most promising method is again radiographic investigation, which would, however, have to be more exact and sensitive than it is to-day. Thus at present we cannot tell for certain why wood gives the same radiospectrogram as a pure cellulose ; are the interference lines of an organic substance too insensitive towards the presence of a foreign substance, and would the latter exhibit its own lines if the method could be sufficiently refined ? Or is the conclusion permissible that the lignin is adsorbed in amorphous form upon the cellulose of the wood ; and if this be not the case, would the amorphous micellæ of the lignin, distributed in some manner in the crystalline structure of the cellulose, make their presence evident by a uniform darkening of the radiogram ? I should prefer to regard the adsorption of the lignin on the cellulose as more probable at present.[2] Connected with this is the general question, whether substances which are adsorbed by a crystalline adsorbent such as cellulose and which themselves tend to crystallize show their own lines in the radiospectrogram, or whether they do not, either because they are only adsorbed in a unimolecular layer or because, if present in thicker layers, they cover the surface in an amorphous form.

Wood, fibres, and starch betray by their polyphasic nature their living origin. Among living organisms this type of structure is doubtless so general, that special proof is needed in each case that a sol or gel present in a living organism contains strictly only micellæ of one kind. With sols such as blood, we are quite accustomed to take into account, along with the micronic particles of the blood corpuscles, sub- and amicrons of the proteins and other colloidally dissolved substances. This is less a matter of course in the case of gels. But here as well it appears to me that account should be taken of the views which assume, say in the plasma membrane, a mosaic of protein and lipoid micellæ (see p. 747). The contents of the cells themselves are also not usually to be regarded as dilute sols. Micellæ of different kinds, and other and larger constituents of the cells, are not by any means to be regarded as freely mobile, but are rather, as in a sol close to the point of gelation, arranged to a great extent closely packed, so that the comparison with a foam,[3] as regards regularity of arrangement, resist-

[1] Kolloidzeitschr. **11**, 1 (1912).

[2] A view at which *H. Wislicenus* has also arrived. Tharandt. forst. Jahrb. **60**, 313 (1909).

[3] See *Rhumbler*, in *Abderhalden's* "Handbuch. der biologischen Arbeitsmethoden," Abt. V, Teil 3, p. 219 *et seq.* (1921).

ance to mechanical disturbance, and so on, is by no means to be rejected. Here also the difficulty of determining the arrangement and distribution of a certain kind of micella inside the cell is met with ; the language of staining experiments with various kinds of organic dyes cannot yet be interpreted in detail in this direction. Also, as a rule they can only be made use of after certain preparative processes, such as fixation, hardening and so on, which produce deep-reaching changes in the constituents of the cell.

ADDENDA

Page 34. The relationship between surface energy and latent heat of vaporization suggested by Stefan has been submitted to a more detailed investigation by Harkins and L. E. Roberts.[1] These authors compare the molar total surface energy (cf. p. 35) with the molar internal latent heat, and assume that the number of molecules present in unit surface is equal to the 2/3 power of the number present in unit volume. It was found that Stefan's assumption, as expressed in the form that the quotient $\frac{\text{molar total surface energy}}{\text{molar internal latent heat}}$ is constant, is incorrect; instead, the value of this expression increases with rise of temperature and is greater for substances, such as methyl and ethyl alcohols, with strongly unsymmetrical molecules, than for those, such as carbon tetrachloride and nitrogen, with symmetrical molecules. The latter fact accords with the view that the molecules of unsymmetrical substances are orientated in the surface (cf. p. 69). The energy necessary to bring an unsymmetrical molecule into the surface is smaller than that required to transport it from the surface into the gas space; for in the latter case the polar ends of the unsymmetrical molecules, which are provided with strong molecular fields, are directed towards the interior, and their large attraction must be overcome, whilst only the attraction between ends with weak molecular fields has to be overcome when the unsymmetrical molecule is brought from the interior to the surface. In the case of substances with symmetrical molecules this difference between the surface and interior of the liquid is not so pronounced, and the energy required to bring a molecule into the surface is not substantially different from that necessary to transport it from the surface into the gas space (cf. also p. 814).

Page 58. Recent theories of the strong electrolytes (cf. p. 49) point to entirely different values of hydration and to a strong hydration of the hydrogen ion; the latter should accordingly resemble the lithium and not the potassium ion. Thus Bjerrum [2] calculates that the $H^{\cdot}$ ion binds 8 molecules of water whilst the $K^{\cdot}$ ion binds none. The resemblance between the behaviour of $H^{\cdot}$ and $Li^{\cdot}$ ions in the coagulation of the distinctly hydrophilic Odén sulphur sol (cf. p. 848 *et seq.*) is in agreement with this.

Page 73. The investigation of Windisch and Th. Osswald,[3] referred to on this page, has now appeared.

Page 96. Harkins and Cheng [4] have measured the interfacial tensions between water and a large number of organic liquids, the surface tensions of the latter, and all related temperature coefficients, and have calculated

[1] Journ. Amer. Chem. Soc., **44**, 653 (1922).
[2] Zeitschr. f. anorg. allg. Chemie, **109**, 275 (1920); further *Schreiner*, *ibid.*, **121**, 321 (1922).
[3] Zeitschr. f. physik. Chemie, **99**, 172 (1921).
[4] Jour. Amer. Chem. Soc. **43**, 35 (1921).

from their results, in addition to the free and total interfacial and surface energies, the free and total adhesion energies. The free adhesion energy is the decrease in free energy which occurs when the surfaces of two liquids disappear and are replaced by a new interface between the two liquids. The total adhesion energy is related to the free adhesion energy as is the total surface energy to the free surface energy (cf. p. 35). Hence the free adhesion energy is given by

$$\mathbf{v} = \sigma_A + \sigma_B - \sigma_{AB}$$

and the total adhesion energy by

$$\mathbf{w} = \left(\sigma_A - T\frac{d\sigma_A}{dT}\right) + \left(\sigma_B - T\frac{d\sigma_B}{dT}\right) - \left(\sigma_{AB} - T\frac{d\sigma_{AB}}{dT}\right).$$

In most cases the total adhesion energy, like the total interfacial energy $\left(\sigma_{AB} - T\frac{d\sigma_{AB}}{dT}\right)$ and the total surface energy, was largely independent of temperature (cf. p. 39). Liquids with strongly unsymmetrical molecules, e.g. heptinene (a hydrocarbon with a triple bond at one end) and heptaldehyde, formed noteworthy exceptions. With these, the temperature coefficient of the interfacial tension $\frac{d\sigma_{AB}}{dT}$ was positive over an appreciable range of temperature, and, in fact, so strongly that the total interfacial energy was negative and dependent on temperature, whilst the free interfacial energy, and hence the interfacial tension, remained positive. According to the relation between surface tension and solubility discussed on p. 70, the increase of interfacial tension with temperature in the case of these liquids corresponds with the decrease in their solubility in water with rise of temperature. The difference between liquids such as hexane, octane, and carbon tetrachloride with symmetrical, and those mentioned above with unsymmetrical, molecules may be characterized as follows: their surface energies, which are always relatively small, differ little, but their adhesion energies differ greatly, being larger in the case of the liquids with unsymmetrical molecules. This can again be explained by Langmuir and Harkins' theory (p. 69). The liquids with unsymmetrical molecules turn their polar, hydrophilic group (unsaturated group, hydroxyl, carboxyl, etc.) towards the water. This is the group with the strongest molecular field; hence the adhesion energy is caused by the strong molecular field. In the interior of the liquid, on the other hand, no decided arrangement exists. Here, the hydrophobic group (CH_3, etc.), which has the weakest molecular field, controls the coherence of the molecules. This is therefore the cause of the small surface energy.

Page 110. Of recent measurements of the adsorption of gases, those by Sceliger,[1] using dehydrated chabasite (a zeolite) as adsorbent, may be specially mentioned. In general, they confirmed the known laws, although some striking peculiarities (e.g., the remarkably strong adsorption of hydrogen) must be noted.

Page 122. No experiments have yet been carried out which permit of a decision between the theories advanced by Langmuir and Polanyi respectively. According to Carver,[2] the adsorption of toluene vapour by glass at 0° can be best interpreted according to Langmuir's views, i.e.

[1] Physik. Zeitschr. **22**, 563 (1921).
[2] Jour. Amer. Chem. Soc. **45**, 63 (1923).

on the basis of a unimolecular layer. On the other hand, Berényi [1] has succeeded in evaluating Berl and Andress's measurements,[2] which relate to the adsorption of various vapours by the active charcoal of the Bayer dye-works, on the basis of Polanyi's theory. The latter, as is well known, is more readily explained on the assumption of a multimolecular layer, although it does not exclude a unimolecular one. It is exceedingly improbable [3] that the condensation of vapours in the capillaries of charcoal or of silicic acid gels is alone capable of explaining adsorption, although this view is sometimes held.[4] In this case the adsorption potential—Polanyi now employs the better term adsorption affinity—would decrease, with rise of temperature, in proportion to the surface energy; further, at a given temperature, a proportionality would exist between the adsorption affinities of different vapours and their surface tensions. Neither holds entirely. Condensation in the capillaries probably only plays a rôle in the neighbourhood of the saturation pressure (cf. p. 163).

Page 143. Explosions of dust, especially of sugar dust, have recently been investigated in detail by Beyersdorfer,[5] who takes into account the adsorption of oxygen on the surface of the extremely fine sugar crystals. It is, however, further essential for the process, that, after the dust has become electrically charged by movement in the air, a spark discharge should take place, and that an explosive combustion should be propagated through the entire dust cloud, provided that the latter is sufficiently dense; the flame produced by the combustion of one particle must be able to ignite the neighbouring particles. With a content of 0·6 g. sugar per cubic centimetre the mean distance is too large.

Page 144. Rideal [6] finds that the reduction of ethylene by hydrogen on nickel surfaces is an example of a reaction in which the velocity is always dependent on the concentration of the reactant present in smaller amount, and is at a maximum when the reactants are present in a certain ratio. He emphasizes that this behaviour is quite to be expected from Langmuir's theory (p. 175) of unimolecular adsorption layers, as also is a maximum in the reaction velocity with rising temperature; this was observed at 137°.

H. S. Taylor and Burns [7] point out the following fact, which is of general importance for adsorption catalysis, regarding this reaction: at a temperature of 130–150°, at which, as mentioned above, the nickel favours the combination of the hydrogen and ethylene most strongly, the adsorption is much smaller than at room temperature, at which the reaction is only just detectable. It is thus quite possible for weak adsorption, or an extensive evaporation of the substance from the surface, to be more advantageous than strong adsorption with the possible formation of inhibitory layers. Hence, in the case of an adsorption reaction in which the adsorption is small, it can on no account be concluded that the latter is not able to exert a greater influence on the process than if it were large.

[1] Zeitschr. f. angew. Chemie, **35**, 237 (1922).

[2] Zeitschr. f. angew. Chemie, **34**, 369, 377 (1921).

[3] According to an unpublished communication from Polanyi. Regarding the theory of gas adsorption, see also *Eucken*, Zeitschr. f. Elektrochem. **28**, 6, 257 (1922); *Polanyi, ibid.* **28**, 110 (1922); *R. Lorenz* and *Landé*, Zeitschr. f. anorg. allg. Chemie, **125**, 47 (1922).

[4] See, for example, *Chaney*, Trans. Amer. Electrochem. Soc. **36**, 91 (1919); *Gustaver*, Kolloidchem. Beiheft. **15**, 185 (1922).

[5] Ber. d. deutsch. chem. Ges. **55**, 2568 (1922); Kolloidzeitschr. **31**, 331 (1922).

[6] Journ. Chem. Soc. **121**, 309 (1922).

[7] Journ. Amer. Chem. Soc. **43**, 1273 (1921).

Page 153 *et seq.* That finely divided metals are able to adsorb gases in the usual sense of the word follows from experiments by H. S. Taylor and Burns (*loc. cit.*). They measured the taking up of gases such as H_2, N_2, CO, CO_2, and C_2H_4 by finely divided Ni, Co, Fe, Pd, and Pt. A parallelism was not, it is true, usually present, but rather a specific affinity. There was, however, a decided decrease in adsorption with rise of temperature, and, in the case of the adsorption of H_2 by Ni and of CO by Cu which were investigated in more detail, a dependence on the pressure resembling the ordinary adsorption isothermal occurred.

Page 155. In view of the small number of measurements of the interfacial tensions of solids, it merits mention that Glasstone [1] has found decided differences in the solubilities of various forms of PbO. He attributes them to differences in the degrees of dispersion, and calculates, in accordance with the considerations on p. 155, the interfacial tension of PbO against normal aqueous NaOH to be 1860 dyn./cm. at 20°.

Page 161. An investigation by Sulman [2] appears to give as complete a theoretical treatment of the flotation process as is at present possible. The following must accordingly be added to p. 161. The amount of oil employed technically is so small that the film which coats the mineral particles is only a few $\mu\mu$ thick; hence the process depends less upon a true displacement than upon wetting. Wetting processes appear, quite generally, to predominate over capillary electrical and colloido-chemical phenomena in importance. But it does not depend alone upon *wettability*, i.e. upon the fact that the gangue, which is more easily wetted, passes into the aqueous phase, whilst the particles of the sulphide ores, which, specially when they are coated with a film of oil, are difficultly wettable by water, pass into the foam. The indefinite nature of the contact angle, its *hysteresis* (cf. p. 162 *et seq.*), is also apparently of especial importance. If the hysteresis of the contact angle is large, this means that any surface of a solid particle which is covered with air will not be immediately wetted during the movement of the particle, although this would happen after a longer period of time; with slight hysteresis, on the other hand, the wetting corresponding with equilibrium is readily attained. Hence the oil, and specially the electrolytes added to the aqueous phase, must be so chosen that the hysteresis is as large as possible in the case of the sulphide ore particles and as small as possible in the case of the gangue.

Page 162. Trustworthy measurements [3] of contact angles increase. The following method has proved of service where the contact angle is large: A plate of the solid is dipped into the liquid and rotated about an axis in the plane of the plate until the liquid cuts the plate horizontally; the angle which the face of the plate forms with the liquid surface is then determined. Bosanquet and Hartley (*loc. cit.*) found by this method values of 106° 57′ at 14° for water on paraffin and 77° at 15° for water on azobenzene; these were in agreement with results obtained on the basis of the height of rise in capillaries. No finite angle of contact can be detected between glass and wetting liquids even when a refined method is employed; we may therefore assume, as has usually been done hitherto, a zero angle of contact. Measurements by Th. W. Richards and Carver [4] are in agreement with this.

[1] Journ. Chem. Soc. **119**, 1689 (1921).
[2] Bull. of the Inst. of Min. and Metall., No. 182 (1919).
[3] *Bosanquet* and *H. Hartley*, Phil. Mag. (6), **42**, 456 (1921); *Sulman*, *loc. cit.* under [2].
[4] Journ. Amer. Chem. Soc. **43**, 827 (1921).

Page 168. It is questionable if the statements of Junck and Schwalbe are correct. In any case, Patrick and F. V. Grimm [1] found that the heat of wetting of a silicic acid gel and water between 0° and 4° is positive and not negative. These authors have also measured the heat of wetting of this gel with respect to benzene, alcohol, carbon tetrachloride, and aniline.

Pages 172 *and* 173. The values (concentration and amount adsorbed) plotted for succinic acid in Figs. 33A and 33B refer to equivalents and not mols.

Page 183. Wo. Ostwald and de Izaguirre [2] point out that the experiments of Gurwitsch can be calculated equally well with the ordinary adsorption isothermal as with the special formula employed by Gurwitsch.

Page 185. In some as yet unpublished experiments, Polanyi and Heyne have investigated adsorption in solution from the point of view of Polanyi's theory, i.e. they have evaluated the adsorption affinity, tested its dependence on temperature, and determined the remaining values, such as heat of adsorption and heat of wetting, which are concerned in a thermodynamical treatment. While in the case of the adsorption of vapours the characteristic curve of adsorption (see p. 126) is independent of the temperature, and the same holds for the curve which represents the dependence of the adsorption affinity on the amount adsorbed, with solutions these curves depend on the temperature in such a manner that they are displaced towards higher values as the temperature rises. Polanyi explains this in the following manner : In the adsorption of vapours, the final and initial states which one considers in a thermodynamical argument are the same, namely, the liquid state. With dissolved substances which, at the same temperature, are present in the initial state undissolved and in crystalline condition, the final state at the interface is, on the other hand, quite different ; they are then probably in the amorphous-solid form, for they do not betray their presence by interference lines in the Debye-Scherrer diagram (cf. p. 811).—They would also, it is true, fail in this respect if they were adsorbed in unimolecular layers.—Hence in a thermodynamical argument an additional energy magnitude, dependent on temperature, must be introduced, namely, the work of fusion ; and it is, in fact, possible to calculate the displacement of the adsorption affinity curve with temperature from the dependence of the work of fusion on temperature. It is further in agreement that, in the adsorption of phenol from aqueous solution at temperatures above the melting-point, the adsorption affinity curve is again independent of temperature.

Page 199. Maleic and fumaric acids and citraconic and mesaconic acids furnish further examples of the relationship between adsorbability and solubility. According to recent experiments by de Izaguirre the more soluble maleic acid is adsorbed to a smaller extent by charcoal than the less soluble fumaric acid ; similarly citraconic acid, which is more soluble than mesaconic acid, is adsorbed to a smaller degree than the latter.

Now, according to the considerations on p. 139, a chemical equilibrium at a surface should be so displaced as to favour the formation of a strongly adsorbable substance. Since maleic can be transformed into fumaric, and similarly citraconic into mesaconic acid, it might accordingly be expected that this transformation would be favoured on the charcoal and would, perhaps, even take place at low temperatures. This has certainly not yet been observed in the case of charcoal, but statements are available which indicate that other adsorbents behave in this manner. According

[1] Journ. Amer. Chem. Soc. **43**, 2144 (1921).
[2] Kolloidzeitschr. **30**, 279 (1922).

to O Loew and Aso,[1] platinum black will transform maleic into fumaric acid at room temperature; perhaps the transformation of these acids into one another in the presence of sulphides and colloidal sulphur, described by Skraup,[2] also depends on an adsorption reaction of this kind.

Page 199. The treatment of adsorption in solutions of several substances has undoubtedly been too greatly simplified. The rules given are doubtless only true in limiting cases. Departures from the described behaviour in which an increased adsorption, and not a displacement, occurred in the presence of a second substance were pointed out on p. 642 in connexion with the experiment of Abderhalden and Fodor. Kruyt and van Duin[3] have obtained similar results. Hence these phenomena require a more detailed investigation.

Page 201. Diverse investigations on the adsorption of electrolytes have not simplified our views concerning this important but complicated phenomenon. Odén and his collaborators[4] have measured the adsorption of a series of inorganic electrolytes on a carefully purified animal charcoal and have found an absolutely equivalent adsorption. They are therefore of the opinion that any observed non-equivalent adsorption is always to be ascribed to an exchange adsorption caused by the substances yielding ash. Nevertheless one must treat this conclusion with caution and allow the possibility of a fission adsorption as mentioned on p. 204 to remain open. For Bartell and Miller[5] describe adsorption experiments with a pure ash-free sugar charcoal in a pure methylene blue solution in which there was, it is true, an equivalent adsorption when small amounts were adsorbed; when, however, large amounts were adsorbed there was a pronounced fission whereby $H^{\cdot}$ ions remained in the solution. They are convinced that this was due to a hydrolytic fission produced by adsorption.

Under these circumstances it appears to me premature to regard the adsorption of electrolytes exclusively as a "chemical" adsorption, as Kolthoff[6] assumes.

Page 220. By means of the adsorption of the radio-elements, Paneth[7] has succeeded in determining more accurately than hitherto the size of the adsorbing surface and the thickness of the adsorbing layer. He investigated the adsorption of thorium B by $PbSO_4$ powder, and measured the decrease in the concentration of the radio-element on shaking with this powder. The solution was either saturated with $PbSO_4$ or contained in addition $Pb(NO_3)_2$. ThB is isotopic with Pb. If the adsorption equilibrium is considered kinetically, the ThB atoms must distribute themselves between the surface and the solution in the same ratio as the Pb atoms for they are, in fact, Pb atoms which have, as it were, been given a dis

[1] Bull. of the Coll. of Agric., Tokyo, **7**, 1 (1906); cited from Chem. Zentralbl., 1906 II, 492.

[2] Wien. Monatsh. **12**, 107 (1891).

[3] *Loc. cit.* p. 318.

[4] *Odén* and *H. Andersson*, Journ. Phys. Chem. **25**, 311 (1921); *Odén* and *Langelius*, *ibid.* **25**, 385 (1921).

[5] Journ. Amer. Chem. Soc. **44**, 1866 (1922).

[6] Kolloidzeitschr. **30**, 35 (1922); see also the objections of *Wo. Ostwald*, *ibid.* **30** 254 (1922), which appear to me to be justified.

[7] Zeitschr. f. Elektrochemie, **28**, 113 (1922); *Paneth* and *Vorwerk*, Zeitschr. physik. Chemie, **101**, 445 (1922).

tinctive mark by means of their radioactivity. Hence the following relation holds :

$$\frac{ThB_A}{ThB_L} = \frac{Pb_O}{Pb_L} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here ThB_A and ThB_L are respectively the number of ThB atoms adsorbed per gram of $PbSO_4$ and the number present in solution, Pb_L is the amount of lead, determined analytically, in the solution, Pb_O the Pb atoms present in the surface per gram of $PbSO_4$ which participate in the exchange adsorption. For one and the same $PbSO_4$ preparation Pb_O was, in fact, constant and independent of the amount of adsorbent employed and of the concentration of Pb ions in the solution. That it is a question of an adsorption in which only the surface of the powder is of influence follows from the fact that the equilibria were established rapidly and reversibly.

Now, it follows from the conception of isotopy that if a definite number of ThB atoms have been adsorbed, in the same proportion in which they stand to the Pb atoms in the solution, then Pb atoms are also to be regarded as adsorbed. Hence the adsorption of Pb can be calculated from the adsorption of ThB ; from experiments with different concentrations of Pb ions, calculated by equation (1), an adsorption isothermal may thus be obtained. This is represented by

$$x = \frac{Oy}{O + y} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which x is the amount adsorbed, y the amount of adsorptive originally present in solution, and O the constant amount of atoms of metal present in the surface.

This equation agrees well with other data. At large concentrations, when O is negligible compared with y, it leads to a saturation ; and it resembles to some extent the adsorption isothermal which may be deduced from Szysykowski's equation on the basis of Gibb's formula (cf. p. 113).

Paneth and Vorwerk [1] have further measured the adsorption of a dye, ponceau red 2R, at a surface which had been measured in the manner just described. Their results showed that, if the molecules of the dye were assumed to be cubes, about 30 per cent. of the surface must be regarded as covered. If, however, they were assumed to be parallelopipeds attached to the surface by means of their large faces, the surface would be covered approximately once. This suggests that, in the present instance, the adsorption film consisted only of one layer of molecules.

Page 226. Experiments by Erich Müller [2] have shown that the decomposition of formic acid into CO_2 and H_2 is only slightly, if at all, caused by the rhodium itself. Osmium has a much greater activity, and a small content of this metal in the Rh preparations is probably the chief cause of their activity. The decomposition is favoured if the osmium is dispersed colloidally to the greatest possible extent.

Page 235. The phenomenon of a substance which possesses no adsorptive power when in true solution gaining this power immediately it has formed larger particles is so important for the theory of adsorption that a further example may be mentioned. P. Karrer [3] found that α-amylose gives no coloration with iodine when in true solution but does so immediately

[1] Zeitschr. f. physik. Chemie, **101,** 480 (1922).
[2] Zeitschr. f. Elektrochemie, **28,** 307 (1922).
[3] Helv. Chim. Act. **4,** 994 (1921).

it commences to crystallize from the solution. The crystals of α-amylose are also coloured blue by iodine.

Page 277. The investigations of Gyemant [1] have now appeared. Baur,[2] in a further paper, has adduced new evidence which, in his opinion, makes it probable that the phase boundary force between liquids is due solely to an adsorption potential difference and not to a distribution of ions. He relies especially on Wild's [3] results, according to which the electrocapillary curves of solutions of capillary-inactive salts in various solvents have their maximum at the same potential. It would actually follow from this that the potential difference resulting from the distribution of ions between the two solvents is zero, provided, however, that the conditions of equilibrium are strictly fulfilled. According to a verbal communication from Gyemant, it would appear questionable if the two solutions were strictly in equilibrium with respect to all the substances, including the Hg salts, present.

Page 282. That alkaloids are very active ballo-electrically [4] is noteworthy in connection with their activity in electrokinesis and coagulation.

Page 314. If the further experiments of Perrin, Volmer, and others, which will be discussed in more detail below (cf. p. 821), are considered, the opinion expressed on this page will appear to be almost certainly correct. Adsorption films are frequently unimolecular, as, for example, in the case of the adsorption of ponceau red by $PbSO_4$ discussed on p. 819. But there unquestionably exist films consisting of two, three, or even more molecular layers. As an example may be mentioned v. Euler's [5] measurements of the adsorption of silver salts on silver and gold powders and especially on gold leaf. Hence a decision regarding the thickness of the adsorption film in any particular case requires a special investigation.

Page 317. There is scarcely a problem more important for the further development of colloidal chemistry than that of the orientation of molecules at an interface.[6] Hence we may quote an example of how, according to Kruyt and van Duin (*loc. cit.*, p. 318), the inhibition or acceleration of a reaction may be explained on the basis of the orientation of the molecules at a boundary surface.

In the interaction between the acid sodium salt of *p*-sulphodibromohydrocinnamic acid and KI according to the equation

$$NaSO_3 \cdot C_6H_4 \cdot CHBr \cdot CHBr \cdot COOH + 2KI = NaSO_3 \cdot C_6H_4 \cdot CH{:}CH \cdot COOH + I_2 + 2KBr$$

an inhibition was observed in the presence of carbon. In the corresponding reaction between dibromosuccinic acid and KI,

$$COOH \cdot CHBr \cdot CHBr \cdot COOH + 2KI = COOH \cdot CH{:}CH \cdot COOH + I_2 + 2KBr,$$

[1] *Freundlich* and *Gyemant*, Zeitschr. f. physik. Chemie, **100**, 182 (1922); *Gyemant ibid.* **102**, 74 (1922).

[2] Zeitschr. f. physik. Chemie, **103**, 39 (1922).

[3] Zeitschr. f. physik. Chemie, **103**, 1 (1922).

[4] *Daubanton*, "Nebelelektrizität physiologisch wirksamer Substanzen, insbesonder der Alkaloide." Dissertation, Utrecht, 1920; cited from Ber. f. d. ges. Physiol. **5**, 11 (1921).

[5] Zeitschr. f. Elektrochemie, **28**, 2 (1922); *v. Euler* and *Hedelius*, Sv. Vet. Akad Afd. f. Kemi, **7**, No. 31 (1920); *v. Euler* and *Zimmerlund*, *ibid.* **8**, No. 14 (1921).

[6] Regarding a further confirmation and extension of Langmuir's experiment (p. 315), see also *Adam* [Proc. Roy. Soc. **99**, A, 336 (1921); **101**, A, 452, 516 (1922); Nature, **107**, 522 (1921)].

an acceleration occurred. The action in the case of the salt of the sulpho-acid may be interpreted, following Langmuir and Harkins (p. 315), as follows : The benzene nuclei have a tendency to lie flat in the surface ; the strongly hydrophilic sulpho-groups will, however, oppose this, since they will project in a decided manner into the water. This will cause the side-chain containing bromine to turn away from the water phase, and since the KI, which is only adsorbed slightly, is present mainly in the water, in which, therefore, the reaction takes place, the position of the reacting groups of the organic substance at the interface is less favourable than in the free solution. The reaction is inhibited by carbon. The carbon chain of the dibromosuccinic acid will also lie flat in the surface. In this case, however, the symmetrically arranged CHBr- and COOH-groups, which are hydrophilic to about the same degree, will be turned towards the water, that is, in a manner equally favourable for the reaction with the KI. The increased concentration produced by the adsorption can therefore cause an acceleration.

Page 318 *et seq.* According to experiments by Hinshelwood and H. Hartley,[1] the rate of formation of nuclei in supercooled melts of organic substances is frequently by no means the true rate of formation ; the process is governed chiefly by the presence of dust originating from the air, the particles of which are colloidally disperse. In favour of this view is the fact that the capacity for supercooling is increased by heating the melts to higher temperatures or by simple ageing. The size of the dust particles is probably decisive for their action as nuclei. If they are so large that they attain, together with the adsorption layer of liquid molecules, a size corresponding with the inoculation threshold (p. 324), crystallization commences immediately ; if they are smaller, it will depend on the same probability conditions which lead to the formation of nuclei whether they acquire the necessary size for the inoculation threshold.

Page 325 *et seq.* According to recent investigations by Volmer [2] our conception of the crystallization velocity, whether of supercooled melts, solutions, or vapours, must now differ considerably from that usually formed hitherto. He allowed, for example, Hg crystals to grow at low pressures from supersaturated vapours and found that, for large increases in size, layers are formed in rapid succession on the crystal face ; these begin at one point and spread with uniform thickness over the whole face. Crystals of PbI_2 in a solution behaved similarly ; in this case it could be recognized from the interference colour that the thin layers formed were of uniform thickness, and that even at the boundary of the layer the difference in colour remained constant. R. Marcelin [3] had previously emphasized that in the crystallization of *p*-toluidine from supersaturated alcoholic solution the growth of the crystals always occurred by the addition of thin layers, as if by deposition.

Volmer concludes from this that the freshly added molecules or atoms do not enter immediately into the crystal lattice but remain in an adsorption layer ; they are able to move without restraint in this layer but, on account of adsorption, are less readily able to move at right angles thereto. This is thus a case of molecular movement in two dimensions instead of in

[1] Phil. Mag. (6), **43**, 78 (1922).

[2] In particular, Zeitschr. f. physik. Chemie, **102**, 267 (1922) ; further *Volmer* and *Estermann*, Zeitschr. f. Physik, **13** (1921) ; *Volmer, ibid.* **9**, 193 (1922) ; Physik. Zeitschr. **22**, 646 (1921).

[3] Ann. d. phys. (9), **10**, 185 (1918).

three.[1] Marc (cf. p. 335) had already arrived at the result that a crystal adsorbed its own molecules. If, now, molecules moving in the adsorption layer collide inelastically, which happens when the energy thereby liberated is taken up by the atoms of the crystal lattice, a crystal nucleus is formed to which the further molecules present in the adsorption layer attach themselves ; hence there is a tangential but not a vertical growth. Since the newly formed thin layers may have different interference colours, it follows that they are not always composed of unimolecular adsorption layers but may consist of multimolecular ones. This is likewise in good agreement with other observations of R. Marcelin.[2] The latter prepared extremely thin laminæ of mica by pressing, following Wood, a leaf of mica on molten selenium and, after solidification, tearing off the latter. An extremely thin lamina of mica adhered to the surface of the selenium ; conclusions as to its thickness were drawn from its interference colour. Calculations of these thicknesses gave values which were definitely multiples of $0{\cdot}7\ \mu\mu$; the thinnest lamina had a thickness of $1 \times 0{\cdot}7\ \mu\mu$, and the thickest one of $16 \times 0{\cdot}7\ \mu\mu$. Since the diameter of a mica molecule may be estimated as about $0{\cdot}7\ \mu\mu$, this means that the layers were 1–16 molecules thick.

Now, according to Volmer, the crystallization velocity depends on the extent to which the adsorption layers are occupied by molecules, that is, on the strength of the adsorption. It is true that no measurements are available of the adsorptive powers of the different faces of a crystal for their own molecules. But Volmer, from certain probable assumptions, arrives at the result that the crystallization velocities of different faces of a crystal may easily have a ratio of 1 to 1,000 or more ; and a ratio of this magnitude is required in order to explain the leaf and needle shaped crystals which are so frequently observed On the other hand, Valeton's theory, discussed on p. 335, is not able to yield this result, unless indeed we are to assume a reflexion of the impinging molecules from the crystal face, which reflexion has never been observed.

The growth of a crystal in a supercooled melt is also attributed by Volmer to this behaviour. The stronger or weaker adsorption on a crystal face is here expressed by a larger or smaller capacity of being wetted by the supercooled melt. It is actually found that the most slowly growing basal face of a Hg crystal is wetted by mercury with a definite contact angle, while the other faces are rapidly covered since the mercury readily spreads on them. The different degrees of wettability of the various faces also explains the fact that the crystal formed from a supercooled drop may grow out beyond the boundary of the drop.

The description on pp. 328 *et seq.* and 336 *et seq.* of the significance of adsorption in the change produced by foreign substances in the crystallization velocity is naturally in good agreement with Volmer's views which have just been discussed.

Page 343 *et seq.* It must be emphasized that Perrin's relation only holds when the emulsion is really sufficiently dilute. If it is more concentrated, it is only true in the highest layers of a vertical liquid column, in which the concentration is small. The latter then increases much more slowly in the lower layers than required by the hypsometric formula and attains a constant

[1] It may be mentioned that *McBain* and *Salmon* [Proc. Roy. Soc. **98, A, 398** (1921)] observed that, on coming into contact with a thread of the coagel, the micellæ of a soap sol adhered to it, but remained in lively one-dimensional Brownian movement along the length of the thread.

[2] Ann. d. phys. (9), **10,** 189 (1918).

end value at a certain depth. Porter and Hedges,[1] who have carried out such measurements, found in the case of the gamboge emulsion which they employed a constant concentration at a distance of about 0·13 cm. from the surface. The hypsometric formula could only be regarded as valid up to a depth of 0·01 cm. Burton and Miss Bishop [2] had previously pointed out that deviations from strict behaviour are to be taken into account with colloidal solutions.

Page 387. In place of the sentence, "Each colloid particle recognized ultramicroscopically forms the apex of a cone of light, the base of which is seen as a diffraction disc," the following should be introduced: "Each particle recognizable ultramicroscopically is a centre of disturbance from which a spherical wave originates. A part of this spherical wave, depending in amount on the aperture of the objective, enters the microscope. This part is made to converge towards the observer by the lens of the microscope, and in the centre of the part of the spherical wave thus cut off an interference disc is formed, the diameter of which depends on the aperture of the objective."

Page 389. Zsigmondy has recently made an important improvement in the immersion ultramicroscope by introducing a small trough, through which the liquid to be investigated can flow, between the two objectives.

Page 389. The statement, "Other types of dark-ground illumination, especially by use of paraboloid condensers, have been applied to ultramicroscopic purposes by Cotton and Mouton, v. Ignatowsky, Jentzsch, and others," is misleading, for the constructions alluded to under these names do not depend on the use of a paraboloid condenser; that of Ignatowsky and Jentzsch recalls rather the cardioid condenser, while Cotton and Mouton employ a method by which the illuminating light is prevented by total reflexion from entering the microscope. The paraboloid condenser was described by Siedentopf [3] after the precedent of Wenham.[4]

Page 404. With crystalline, non-spherical particles the twinkling is occasionally so strong that it is visible macroscopically and without further magnification. I. Traube and Klein [5] found this especially with ultramicroscopic particles of $PbCO_3$. It appeared as if one could see the movement of the particles. This is naturally not the case. The illusion is caused by other particles continually flashing into view and causing it to appear as if one and the same particle were undergoing changes in position. It may be mentioned that Siedentopf [6] had previously given an explanation of the twinkling in the case of non-spherical particles which are larger in one direction than the wave-length of light.

Page 408 *et seq.* The view expressed by Weigert (p. 411) that the double refraction of sols with non-spherical particles is due rather to aggregates of amicronic particles, in which the latter are separated from one another by amicronic distances, than to particles which one can see in the ultramicroscope, appears to be confirmed by recent experiments. This is shown especially by an unpublished investigation by Schuster of the behaviour, described on p. 411, of benzopurpurin sols. By warming benzopurpurin with water in sufficiently large dilutions, sols may be obtained which show

[1] Trans. Farad. Soc. **18,** 1 (1922).
[2] Proc. Roy. Soc. **100,** A, 414 (1922).
[3] Zeitschr. f. wissensch. Mikrosk. **24,** 104 (1907).
[4] Trans. Microsc. Soc. **4,** 55 (1856).
[5] Kolloidzeitschr. **30,** 19 (1922); Physik. Zeitschr. **23,** 171 (1922).
[6] Zeitschr. f. wissensch. Mikrosk. **29,** 1 (1922).

no double refraction at room temperature even after a long time. If, however, solutions of electrolytes are added in such a manner that their concentration in the liquid is much smaller than that necessary to produce flocculation, a double refraction appears in course of time. The concentrations of different electrolytes which are necessary to produce, under comparable conditions, a certain double refraction follow regularities (influence of the valency of the kation, etc.) similar to those with which we are familiar in the case of coagulation. We are thus dealing with the first stage of a coagulation which does not become evident externally but does so in the double refraction. By heating, the double refraction again disappears ; and this phenomenon also entirely follows the regularities which one would expect for the peptization of flakes (cf. p. 470 *et seq*). None of these changes can be recognized ultramicroscopically ; the particles remain amicronic while they take place.

In agreement with this are the observations of Szegvári [1] on V_2O_5 sols using a cardioid ultramicroscope with a so-called azimuth diaphragm, i.e. a rotatable slit diaphragm which only allowed rays of a certain azimuth, hence in a direction perpendicular to the optical axis of the microscope, to enter the cardioid condenser.

According to the argument on p. 406, only rods which lie in the plane of observation at right angles to the illuminating rays can then be seen. In an old, strongly doubly refracting, fairly concentrated V_2O_5 sol, patches of bright and dark spots are seen ; on rotating the azimuth diaphragm through 90°, the bright spots become dark and the dark ones bright. Hence the V_2O_5 sol is filled chiefly with aggregates of submicronic or amicronic particles. Single large needles, usually with their longitudinal axes in the same direction as those of the aggregates, are seen ; these, however, manifestly do not form the chief part of the sol, nor have they a decisive effect on its behaviour.

It is true that with the increase, in course of time, of the double refraction of a V_2O_5 sol a great change in the ultramicroscopic picture is observed. Ostermann [2] has confirmed this by careful measurements. With a fresh sol he found only small submicrons ; after three months fine needles were present, and after six months large needles. At the same time the number of visible particles increased, a sign that many amicrons were present from the beginning. Hence it is quite probable that, as in the behaviour of the benzopurpurin sols just discussed, the amicrons are of chief importance for the strength of the double refraction ; the change recognizable ultramicroscopically might only be a sign of the changes taking place simultaneously in the amicrons.

Björnståhl [3] has published a detailed paper concerning the double refraction of gold sols mentioned on p. 407.

Errera [4] has discovered a remarkable property of V_2O_5 sols. He investigated the dielectric constant of these sols by Nernst's method and found that old, strongly doubly refracting sols have a very large dielectric constant. Thus an approximately 1·4 per cent. sol, which was a year old, had a dielectric constant of 400 ; in order to attain a value of 83, that is, approximately that of water, it was necessary to dilute it 128 times. A 0·12 per cent. sol

[1] Physik. Zeitschr. **24**, 91 (1923).
[2] "Über kolloidales Vanadinpentoxide." Dissertation, Göttingen, 1921. Jahrb. d. philos. Fakultät in Göttingen, 1921, p. 265.
[3] Phil. Mag. (6), **42**, 352 (1921).
[4] Kolloidzeitschr. **31**, 59 (1922) ; **32**, 157 (1923).

which was freshly prepared and hence showed scarcely any double refraction was diluted to 0·012 per cent. for the investigation; on the first day this had a dielectric constant of 74·7, which increased in 20 days to 112·4. The increase in the dielectric constant manifestly runs parallel to that of the double refraction. It can be regarded as certain that the particles in these experiments were oriented by the alternating current parallel to the direction of the current. What change in capacity, leading to a change of this kind in the dielectric constant, is thereby produced, remains undecided.

Page 413 *et seq.* Far more generally than I formerly supposed must the particles of colloidal solutions be regarded as crystalline and not amorphous. When, as is frequently the case, they are formed as precipitates by reactions in solutions, the following two circumstances are, according to Haber,[1] mainly responsible for the process. The resulting molecules of the difficultly soluble substance unite with a certain *rate of aggregation*, and the irregular aggregates thus formed gradually assume a lattice arrangement with a certain *rate of arrangement*. The rate of aggregation corresponds to the coagulation velocity, and the rate of arrangement to the rates of formation of nuclei and of crystallization, according to the sketch on p. 459 of the probable processes which occur in the formation of precipitates. The competition between the rates of aggregation and arrangement determines whether the colloidal particles are amorphous or crystalline. If the rate of aggregation is large and that of arrangement small, the particles will at first be amorphous and will become crystalline only after a long time; if the rate of arrangement is also large, it is impossible to obtain amorphous particles. Hence it is to be expected that a precipitate is more likely to possess amorphous properties when it is produced rapidly than when it is formed slowly. The precipitates of $Al(OH)_3$ and $Fe(OH)_3$ which are formed rapidly by the addition of ammonia to the corresponding salt solutions should thus be amorphous, whilst the micellæ in Al_2O_3 and Fe_2O_3 sols, which are formed slowly by hydrolysis, should be crystalline. This was actually the case. When investigated by Debye and Scherrer's method, the precipitates proved to be amorphous whilst the particles of the sol gave interference lines. In the case of gold, the rate of arrangement is so large that in no case, not even when precipitated as rapidly as possible from solution, was it obtained amorphous.

The dipolar character of the molecule appears to be an important factor in controlling the magnitude of the rate of arrangement. If it is strongly marked, as, for example, in the case of the sulphides HgS, ZnS, CdS, or of the halides AgCl, AgBr, AgI, the crystalline character is favoured both in precipitates and in colloidal particles. If the dipolar character is not pronounced, as with the hydroxides of zirconium and thorium, even the colloidal particles prove to be amorphous and not crystalline. Further, the particles of sulphur and selenium sols show no interference lines.

It may also be mentioned that the difference between the rates of aggregation and of arrangement is distinctly perceptible with the benzopurpurin sols discussed on p. 823. The double refraction, the formation of which depends on a sufficiently large rate of arrangement, only appears with slow coagulation. If, on the other hand, the sol is rapidly flocculated with a large concentration of electrolyte and then peptized by washing with water, it shows no double refraction: the rapidly formed flakes are at first arranged too irregularly and, provided they are not allowed to age, do not give doubly refracting particles even in dilute solution.

[1] Ber. d. deutsch. chem. Ges. **55**, 1717 (1922).

Page 416. Convenient methods for the measurement of the C.V. have been developed by Wo. Ostwald and Fr. V. v. Hahn.[1] They follow the change in density of a sol during flocculation by placing the coagulating sol in the wide limb of a U-tube, the narrow limb of which contains water as liquid for comparison; the heights of the liquid columns in the two limbs are inversely proportional to the densities. Hence one reads the position of the water in the narrow limb. Wiegner [2] had previously employed an arrangement of this kind for the analysis of soils. A second apparatus recommended by Wo. Ostwald and Fr. V. v. Hahn is still more sensitive. They measure the change in density of the liquid undergoing coagulation by the change produced in the volume of a confined gas. An investigation by Hatschek [3] may be referred to with respect to a colorimetric method for following the coagulation of a gold sol.

Page 418 *et seq.* Recent experiments by Matsuno [4] indicate that, in limiting cases, an equivalent, equally strong adsorption may really be ascribed to nearly related cations, and that the relationship represented in Figs. 100 and 101 (pp. 425 and 426) does actually hold good. He investigated the coagulation of an As_2S_3 sol by salts of a large number of cobalt bases. These may undoubtedly be regarded as nearly related. Further, they are presumably all salts of strong bases[5] and hence are largely dissociated. Matsuno carried out the measurements rapidly in order that a certain sensitivity to light of the mixture of the As_2S_3 sol and cobalt salt need not be taken into account. Further, a relatively small amount of As_2S_3 sol was flocculated by an excess of cobalt salt, so that the amount a adsorbed may probably be neglected in comparison with the flocculation value γ. Equation I (cf. p. 425) in the form

$$a = \alpha\gamma^{\frac{1}{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

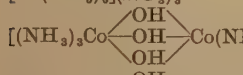
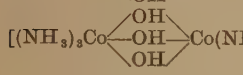
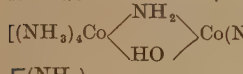
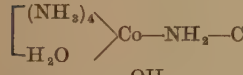
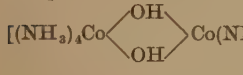
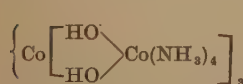
proved, in fact, to be correct when the values $1, \frac{1}{2}, \frac{1}{3} \ldots \frac{1}{6}$, or $6, 3, 2 \ldots 1$, which should be proportional to the true a-values, were substituted for a for uni- to sexi-valent cations respectively. Table 193 contains the observed values and Table 194 the values which were calculated from equation (1) in the manner just described.

Fajans and v. Beckerath,[6] on the basis of the argument first developed by Paneth and Horowitz (cf. p. 220) in connexion with the adsorption of the radio elements, discuss in detail the charge of colloidal particles and the taking up of ions by them. Among other things, they point out that the amount of adsorption depends largely on the degree of insolubility of the adsorbed salt; further, that equivalent amounts of cations (or anions) produce the same discharging effect only so long as their distance from one another in the surface of the colloidal particles is sufficiently large. They further consider the possibility that the adsorbed ions are, in part, dehydrated in the surface. On this perhaps depends the curious distinction mentioned on p. 427 between various sols, namely, that the lyotropic series appears with some but not with others. Whether these considerations, which were first discussed in connexion with AgCl sols, may be applied to all colloidal

[1] Kolloidzeitschr. **30,** 62 (1922).
[2] Landw. Versuchsstat. **91,** 41 (1919).
[3] Trans. Farad. Soc. **17,** 499 (1921).
[4] Journ. of the Coll. Scien. Tokyo **41,** No. 11 (1921); see also Freundlich, Kolloidzeitschr. **31,** 243 (1922).
[5] Cf. *Lamb* and *Yngve*, Journ. Amer. Chem. Soc. **43,** 2352 (1921).
[6] Zeitschr. f. physik. Chem. **97,** 478 (1921).

TABLE 193

Coagulation of As_2S_3 Sols by Complex Cobalt Salts

Electrolyte.		Coagulation Value γ (micromols per litre).
$[Co(NH_3)_4C_2O_4]Cl$		6,670
$\frac{[Co(NH_3)_4(NO_2)^{(1)}_{2(6)}]_3[Co(NO_2)_6]}{3}$		6,000
$[Co(NH_3)_4(NO_3)^{(1)}_{2(3)}]Cl$		5,330
$\frac{[Co(NH_3)_4CO_3]_2SO_4}{2}$		5,330
$[Co(NH_3)_4(NO_3)^{(1)}_{2(3)}]\ [Co(NH_3)_2(NO_2)_4]$		5,330
$[Co(NH_3)_4(NO_2)^{(1)}_{2(6)}]Cl$		4,670
$[Co(NH_3)_4CO_3].\frac{1}{2}H_2O$		4,670
	Mean	5,330
$[Co(NH_3)_5NO_2]Cl_2$		400
$[Co(NH_3)_5NO_2]\ [Co(NH_3)_2(NO_2)_4]_2$		400
$[Co(NH_3)_5SCN]Cl_2$		333
$[Co(NH_3)_5Cl]Cl_2$		333
$\frac{[Co(NH_3)_5Cl_2]_2(HSO_4)_2SO_4}{2}$		333
	Mean	333
$[Co\ en_3]Cl_2$		80
$\frac{[Co(NH_3)_5H_2O]_2(SO_4)_3.3H_2O}{2}$		80
$[Co(NH_3)_6]Cl_3$		66·7
$[Co(NH_3)_6](NO_3)_3$		66·7
		53·3
		53·3
	Mean	66·7
$[(NH_3)_5Co—NH—Co(NH_3)_5]Cl_4$		20·8
		18·8
		18·8
		16·7
	Mean	18·8
		4·2

particles appears to me, from unpublished experiments by Hentschel, perhaps to require testing. Hentschel studied the effect of electrolytes on electrosmosis, us ingdiaphragms of difficultly soluble powders, and found that when these were composed of difficultly soluble salts such as AgCl, $BaSO_4$, and $PbCrO_4$, Paneth and Horowitz's relation was entirely confirmed. With sulphides such as PbS, however, the influence of the degree of insolubility of the resulting sulphides became quite subsidiary to the capillary-active influences such as strong effect of dyes, etc.

TABLE 194

Dependence of the γ-values on the Valency of the Cobalt Ions

$$a = 0{\cdot}6887\ ;\quad \frac{1}{n} = 0{\cdot}2534$$

Valency.	γ (obs.) (micromols per litre).	(calculated) (micromols per litre).
1	5,330	5,130
2	333	333
3	67	67
4	19	22
6	4·2	4·3

An investigation by Mukherjee,[1] which deals with the question of the charging and discharging of colloidal particles, considers, in particular, the influence of valency. I should like, at present, to give preference to Fajans and v. Beckerath's treatment of the subject.

Page 430. Unpublished measurements by Buchler have shown that sols with reversed charges (As_2S_3 sols with charge reversed by dyes such as malachite green, Au sols with charge reversed by dyes and also with $Th(NO_3)_4$) do, in fact, in the upper non-flocculation zone, completely resemble a sol with a corresponding charge, that is, in the cases mentioned, a positive sol. Coagulation accordingly depended on the nature of the anion, i.e. on its adsorbability and valency. It was further found that the flocculation values were, as regards their magnitude, almost independent of the concentration of the electrolyte producing the reversal of charge, which is accounted for by the charge on the particles of the reversed sol being largely independent of this concentration. By means of kataphoretic experiments the ζ, c curve was determined, and it was found that the piece CDE of Curve 5 in Fig. 49 (p. 258), which corresponds with the upper non-flocculation zone, was quite horizontal.

Page 432. Fricke [2] points out that, in addition to the attractive force between colloidal particles, another circumstance may favour the association of discharged particles. If two particles approach one another very closely, the number of liquid molecules remaining between them may be so small that the number of their impacts is greatly diminished as compared with the impacts of the molecules outside the particles. Hence the pressure resulting from the impacts and tending to drive the particles apart is smaller than that due to the external impacts which forces them together.

Page 435 *et seq.* Since the flocculation of As_2S_3 sols has been investigated from so many directions, it may be pointed out that Boutaric and Vuillaume [3] have measured the rate of coagulation of such sols. They followed the change in transparency by a spectrophotometric method. In agreement with v. Smoluchowski's view (cf. p. 436) there was no autocatalytic course, but, from the commencement, a strong increase in the absorption of light. It appears to follow from their curves that, in agreement with Zsigmondy and v. Smoluchowski's view, a finally constant rate of rapid coagulation is

[1] Trans. Farad. Soc. **16,** 103 (1921); Phil. Mag. (6), **44,** 321 (1922).
[2] Zeitschr. f. physik. Chem. **95,** 441 (1920); **97,** 464 (1921).
[3] Compt. rend. **172,** 1293 (1921); **173,** 229 (1921); **174,** 1351 (1922).

reached with increasing concentration of electrolyte. In the region of slow coagulation the increase with the electrolyte concentration is, in accordance with the treatment on p. 442 *et seq.*, extraordinarily large. The behaviour of the temperature coefficient is peculiar. When coagulated with univalent cations, the velocity decreases with rise of temperature; with bivalent ions it increases with the temperature; while with $Al^{...}$ ions it is only slightly dependent on the temperature. The similar results of Mukherjee (p. 466) may be recalled.

Page 447 *et seq.* Szegvári observed the following remarkable phenomenon during the coagulation of concentrated Fe_2O_3 sols (6–10 per cent.) with electrolytes in concentrations which only coagulate slowly. The sol sets to a paste-like jelly; on shaking this liquefies again completely, but, if allowed to stand without disturbance, again becomes solid with a constant velocity depending on the temperature and the concentration of electrolyte. This process may be repeated as often as desired during several months. The rate of solidification completely follows the laws for the rate of slow coagulation; it increases exceedingly rapidly with the electrolyte concentration. Its temperature coefficient is remarkably large.

Page 453 *et seq.* Whilst adsorption reversal only permits the changes occurring during the ageing of precipitates to be followed incompletely and indirectly, O. Hahn, in some unpublished measurements, has utilized a method which is anyhow more likely to give a numerical idea of the extent of the surface of a precipitate at any moment, although there are still difficulties in determining its absolute extent. He produced precipitates, such as $Fe(OH)_3$, $Al(OH)_3$ in solutions containing a radio element, such as radiothorium, which emits an emanation; the precipitates hence contained, as a result of adsorption, some radiothorium. They were then filtered, submitted to different kinds of treatment and stored, for example, after or without ignition or in a dry or moist condition, determinations of the rate of emission of emanation being made frequently. It was found that all circumstances which favoured a large surface (fresh precipitation, precipitation in the cold, absence of ignition) caused a high rate of emission, whilst ageing, ignition, etc. caused this rate to decrease. With large surfaces, the emanation is readily able to diffuse out of the particles. On the other hand, with the formation of the ordered lattices of crystalline particles, it is more or less enclosed and can only diffuse slowly out of the particles or is practically unable to do so at all. This explanation presupposes that the adsorption of the emanation by the surface of the particles may be neglected, which appears probable from what has been stated earlier (cf. p. 121).

Page 455. Wagner's theory of slow hydrolysis has been well confirmed in one respect by Tian.[1] The latter showed that the increase in the conductivity of $FeCl_3$ solutions does not occur when the particles are prevented from coalescing by the addition of a small quantity of gelose to the solutions. But he further showed that adsorption reversal is not the sole cause of the slow hydrolysis. The entire salt is by no means completely hydrolysed at the outset, as Wagner assumed. On the contrary the reverse reaction, in which the colloidal hydroxide forms a salt with the acid, quickly comes into play, so that one is dealing with a hydrolytic reaction in which the base (or acid) which has separated in colloidal form takes part. This reaction should be of general significance for the behaviour of hydroxide sols.

Page 456. In the ageing of Pt and Pd sols, which is measured by their catalytic activity towards hydrogen peroxide, there is at first an increase

[1] Journ. d. chim. phys. **19**, 190 (1921); Kolloidzeitschr. **31**, 165 (1922).

in this activity, which is then followed by a decrease. This behaviour is referred to the action of oxygen.[1]

Page 457. Weiser [2] has investigated in detail the effect of the rate of addition of electrolyte on the flocculation of sols. His explanation of the phenomenon agrees in essential points with that given on p. 457 *et seq.*

Page 462. The statement that non-electrolytes do not coagulate hydrophobic sols requires limitation. According to experiments by Klein,[3] capillary-active substances, such as the higher alcohols and fatty acids, do not by themselves flocculate negative sols such as As_2S_3 sols ; they do so, however, when they are added in alcoholic solution, care being taken that the aqueous solution is supersaturated with the capillary-active substance. This was not observed with positive sols such as those of Fe_2O_3 and Al_2O_3. One might, with Klein, consider that the capillary-active substance separates in colloidally disperse form, and that the effect is really due to the interaction of two sols. It must be confessed that there can probably be no question of the flocculation of oppositely charged sols, since one can hardly ascribe a positive charge to the micellæ of these organic substances. It must therefore be a case of the mutual coagulation of similarly charged flakes of different kinds (cf. pp. 476 and 481).

Page 465. As follows from equation (1) on page 465 and equation (7) on page 434, the specific coagulation time θ should, at different temperatures, be proportional to the expression $\frac{\eta}{\tau}$. Lachs and Frl. Goldberg [4] have confirmed this relation for gold sols between 0 and 70°.

Page 467. Recent experiments by F. L. Browne and J. H. Mathews [5] show that the true heat of coagulation of Fe_2O_3 sols is also small. A large evolution of heat was only observed when the sol contained appreciable amounts of $FeCl_3$.

Page 480. In connexion with the adsorption of the micellæ of hydrophobic sols, attention must be drawn to a curious phenomenon which has been investigated by I. Traube and Klein.[6] They found, in the first place, that saturated or very concentrated aqueous solutions of many difficultly soluble substances, such as amyl alcohol and aniline, contain these substances in the form of submicronic particles. A series of other data also points, in fact, in the same direction. Hence it was surprising to find that the particles of such colloidal solutions concentrate at various interfaces (against air, oil, or silver) when they are capillary-active, but do not do so when they are capillary-inactive. Thus, a concentration was observed with particles of amyl alcohol, octyl alcohol, xylidine, etc., but not with those of gold and Al_2O_3 sols. The particles remain freely mobile at the interface ; the distance from the interface at which uniform distribution commences often amounts to many μ. The latter fact is difficult to reconcile with what would otherwise be expected. It does not appear, however, to be excluded that the whole phenomenon is caused by a source of error which has not yet been considered. It may further be mentioned that, in contrast to a concentration of this loose nature, one of another kind has also been observed. Thus,

[1] Gregorio de Rocasolano, Compt. rend. **171,** 301 (1920).
[2] Journ. Phys. Chem. **25,** 399 (1921).
[3] Kolloidzeitschr. **29,** 247 (1921)
[4] Kolloidzeitschr. **31,** 116 (1922).
[5] Journ. Amer. Chem. Soc. **43,** 2336 (1921) ; with regard to the heat of coagulation, see also Fricke [Zeitschr. f. physik. Chem. **101,** 185 (1922)].
[6] Kolloidzeitschr. **29,** 236 (1921) ; Biochem. Zeitschr. **120,** 111 (1921).

particles of xylidene adhere quite firmly to the surfaces of erythrocytes.[1]

Page 485. Statements [2] that light, X-rays, and other types of rays act upon colloidal solutions are becoming more and more numerous, and before long a separate chapter on photochemistry and colloidal chemistry [3] will doubtless be required. There exists here, however, as in photochemistry generally, the difficulty of referring observations to simple laws. One point, which perhaps has general significance, may be mentioned. According to Haber and Zisch [4] and Kautsky and Zocher,[5] chemiluminescence is closely connected with the fluorescence of one kind of molecule present. Chemiluminescence may actually be regarded as a fluorescence excited by the chemical energy from molecules reacting in the immediate vicinity instead of by light. The necessary close proximity is present, in particular, at interfaces during adsorption, and hence, according to Kautsky and Zocher, heterogeneous structures actually appear to favour the appearance of chemiluminescence.

Page 523 *et seq.* The difficult question as to why neutral and alkaline solutions of many radio elements behave in many respects like colloids is brought nearer to solution by the experiments of Lachs and Frl. Wertenstein.[6] They found that neutral and alkaline solutions of polonium or radium D and E contained in a vertical tube with a length of 58 cm., showed, even after a short time, a greater concentration of the radio element in the lower part of the tube. If we assume that this is due to a Perrin equilibrium (cf. p. 343 *et seq.*) and that the micellæ which are in equilibrium have a density of 2, calculation of their size gives a value of about 10 $\mu\mu$. It is impossible, from the amount of radioactive substance present, for the entire mass of such large particles to consist of the radioactive element. We therefore arrive at the result, which agrees with Zsigmondy's assumption (cf. p. 525), that the radio elements are adsorbed by dust or other colloidal particles present in the liquid, and that this makes it appear as if we are dealing with colloidal radio elements. That radio elements are adsorbed, for example, by filter paper, that the charge of the latter is of influence in this adsorption, and that electrolytes exert an influence in the direction in which they change the charge in electrokinetic experiments, results from measurements by Lachs and Herszfinkel.[7] Since the same properties of ions which cause coagulation are also responsible for their influence on the charge in electrokinetic experiments, it is comprehensible that the adsorption of radio elements by dust particles is changed by ions in the same manner as if the solutions of the radio elements were coagulated by the ions.

Cranston and R. A. Burnett [8] describe a " colloidal behaviour " of non-acid solutions of thorium B and C.

Page 527 *et seq.* Recent experiments by J. Lindemann and Svedberg [9]

[1] Biochem. Zeitschr. **130**, 477 (1922).

[2] See, among others, *Spear, P. F. Jones, Neave,* and *Shlager,* Journ. Amer. Chem. Soc. **43**, 1385 (1921); *Schwarz* and *Friedrich,* Ber. d. deutsch. chem. Ges. **55**, 1040 (1922); *Ganguly* and *Dhar,* Kolloidzeitschr. **31**, 16 (1922); *Cluzet* and *Kofman,* C. R. d. séanc. d. l. soc. d. biol. **86**, 49 (1922), cited from Ber. über d. ges. Physiol. **12**, 331 (1922); *Audubert,* Ann. d. phys. (9), **18**, 5 (1922).

[3] Such a treatment is given by *Schaum,* Kolloidzeitschr. **31**, 258 (1922).

[4] Zeitschr. f. Physik. **9**, 302 (1922).

[5] Zeitschr. f. Physik. **9**, 267 (1922); further, Die Naturwissenschaften, **11**, 194 (1923).

[6] Physik. Zeitschr. **23**, 318 (1922).

[7] Journ. d. phys. et le Radium (6), **2**, 319 (1921).

[8] Journ. Chem. Soc. **119**, 2036 (1921).

[9] Kolloidzeitschr. **29**, 1 (1921).

confirm the view advocated on p. 527 *et seq.* that the so-called critical temperature of flocculation is a kinetic phenomenon. It is a consequence of the diverse influences of temperature, size of particle, etc., on the coagulation velocity.

Page 539 *et seq.* Seifriz [1] has been able to measure directly the rigidity, not only of gels, but also of very dilute sols. He placed in them a small nickel particle (usually of about 18 μ diameter), caused this to be attracted by the point of an electromagnet external to the solution, and followed its movement under the microscope. It was displaced under the influence of the magnetic force, but, when this did not act for too long a time, returned to its original position. From the displacement of the particle measured in this way, conclusions could be drawn regarding the modulus of elasticity and the elastic limit of the sol or gel. An elasticity was observed even in a 5 per cent. solution of light-filter gelatin (of the Höchster Farbwerke) and in a 0·1 per cent. sodium stearate solution; further, in a V_2O_5 sol (0·9 per cent.) and in a 0·025 per cent. solution of benzopurpurin which had become doubly refracting under the influence of a content of $BaCl_2$ of 0·1 millimol per litre. Glycerine and a concentrated solution of cane sugar were completely inelastic. It was remarkable that sodium oleate solutions, in contrast to the strongly elastic stearate solutions, were inelastic. The modulus of elasticity increased greatly and steadily during the transition from sol to gel. The elastic limit showed a pronounced maximum in the region of the soft gel, and hence during the transition from sol to gel. Whilst liquids which show no elasticity obey Poiseuille's law in determinations of the viscosity, large departures appear with elastic liquids immediately one passes to small pressures. The influence of the elasticity of the doubly refracting sols of V_2O_5 and benzopurpurin also appears in the fact that the double refraction does not immediately disappear after stirring.

Page 563. The colour of emulsions at times originates from that peculiar colour phenomenon, investigated by Christiansen,[2] which occurs when two phases which, whilst their dispersion is appreciably different, have the same refractive index with respect to one colour, are intimately mixed. Only that light for which the refractive index is the same passes undisturbed through both phases; light of other colours is refracted and reflected. Bodroux [3] and especially H. N. Holmes and D. H. Cameron [4] have prepared such coloured emulsions, for example, by emulsifying glycerine in a mixture of acetone and benzene with nitrocellulose as emulsifying agent.

Page 564. McBain and his collaborators [5] have continued their investigations of soap solutions. Of the results the following may be mentioned. The addition of higher fatty acids to solutions of salts of higher fatty acids causes a large diminution in the truly dissolved portion and an increase in the colloidally dissolved; the colloidal part is an acid soap (cf. p. 568) which McBain regards rather as a complex compound (in the sense of Werner's theory) of fatty acid and salt of fatty acid [6] than as an

[1] Zeitschr. f. physik. Chem. **104,** 233 (1923).
[2] Wied. Ann. **23,** 298 (1884).
[3] Compt. rend. **156,** 772 (1913).
[4] Journ. Amer. Chem. Soc. **44,** 71 (1922).
[5] *McBain,* Miss *Taylor,* and Miss *Laing,* Journ. Chem. Soc. **121,** 621 (1922); *Salmon, ibid.* **121,** 711 (1922); Miss *Flecker* and Miss *Taylor, ibid.* **121,** 1101 (1922); *McBain* and *A. J. Burnett, ibid.* **121,** 1320 (1922); *McBain* and Miss *Norris, ibid.* **121,** 1362 (1922); Miss *Norris, Falkner,* and *Price, ibid.* **121,** 2161 (1922); *McBain* and *Jenkins, ibid.* **121,** 2325 (1922); Miss *King,* Journ. Soc. Chem. Ind. **41,** 147 (1922).
[6] *McBain,* Miss *Taylor,* and Miss *Laing, loc. cit.* under [5].

adsorption compound. The behaviour of cetyl sulphonic acid and its salts (cf. p. 569) and that of related acids was also investigated in more detail and was, in fact, found to agree largely with that of soap solutions.[1]

Page 573. The apparently exceedingly complicated question of the stability of lyophilic sols has commenced, especially after recent experiments by Kruyt,[2] to disentangle itself. As far as one can see, the point of view which was regarded as useful first by Kruyt, and then by myself on the basis of Scholz's [3] investigation (cf. p. 615 *et seq.*), has proved correct.

Two influences, which are largely independent of one another, are frequently superimposed. The first is capillary-electrical, and hence is the stability caused by the charge such as appears alone with decidedly hydrophobic sols. The second is that of hydration or solvation; this is also apparent with true solutions as true solubility. Kruyt and de Jong were able to separate these two influences in the case of agar sols. Small concentrations of neutral inorganic electrolytes cause a decrease in the viscosity of the sol; this decrease is independent of the nature of the anion and is conditioned solely by the valency of the cation, exactly as in the coagulation of negative hydrophobic sols. The explanation of this is that the micellæ possess an electric charge which, in accordance with Smoluchowski's argument (cf. p. 369), increases the viscosity of the sol. The experiments were carried out above 40° in a range of temperature in which Poiseuille's law is valid; hence the viscosity is a true one (cf. Seifriz's experiments mentioned on p. 832).

The sol has been discharged by the addition of the small amounts of electrolytes. That it does not resemble a hydrophobic sol in becoming unstable is due to the fact that the stability conferred upon it by the hydration remains effective. If a dehydrating substance, such as alcohol or acetone, is now added, the sol is coagulated, since water is removed from the micellæ, which consequently become unstable. If, on the other hand, water is removed from the micellæ by means of alcohol or acetone without the previous addition of electrolytes, the sol remains stable. Its stability, however, now depends solely on the charge of the micellæ; it has become hydrophobic. It is readily coagulated by electrolytes according to their valency and, in contrast to the original aqueous sol, the micellæ are clearly discernible in the ultramicroscope, since the difference between the refractive indices of micella and intermicellar liquid has become much larger owing to the removal of water from the former. Kruyt emphasizes that similar relations also prevail with other sols such as those of gelatin. It is naturally likewise possible that the other limiting case, in which stability is, from the outset, caused solely by hydration, may exist.

Page 583. In addition to the action of the oppositely charged colloidal ions, which has hitherto been preferentially considered in connexion with the sensitization of a sol, a further circumstance must be taken into account with respect to this phenomenon. This advance is also connected with the investigation of Kruyt (*loc. cit.*) just mentioned. He found that tannin causes many hydrophilic sols, such as those of agar, gelatin, and starch, to become hydrophobic, that is, it sensitizes them. In order to explain this, he assumes, in accordance with the views of Langmuir and Harkins (cf. p. 315), that tannin possesses polar properties, the carbon chain of the

[1] Miss *Norris, Falkner,* and *Price, loc. cit.* p. 832.

[2] *de Jong,* "Het. Agarsol." Dissertation, Utrecht, 1921. *Kruyt* and *de Jong,* Zeitschr. f. physik. Chem. **100,** 250 (1922); *Kruyt,* Kolloidzeitschr. **31,** 338 (1922).

[3] *Freundlich* and *Scholz,* Kolloidchem. Beiheft. **16,** 234 and 267 (1922).

glucose being more hydrophilic, and the phenol groups of the digallic acid residue more hydrophobic. He further assumes that, during adsorption, the more hydrophilic side of the tannin faces the hydrophilic micellæ; the more hydrophobic side will then be turned towards the water so that the complex formed from micella and tannin will, as a whole, be hydrophobic. A sensitization of this kind must be considered in those cases in which a hydrophilic sol which does not possess an amphoteric character sensitizes both positive and negative micellæ. Thus, Brossa [1] found that tannin sensitizes not only the positive sol of night blue but also the negative sols of alkali blue, benzazurine, etc. Sols of the dyes are obviously intermediate between hydrophilic and hydrophobic sols, and the possibility exists that they may be sufficiently hydrophilic for the tannin also to turn its hydrophilic side towards the dye particles.

According to Brossa, serum euglobulin behaves towards dye sols in a manner quite similar to that of tannin. It sensitizes the positive sol of night blue as well as the negative sols of Congo red, benzopurpurin, etc.; that is, the sols of these dyes peptize electrolyte-free globulin suspensions to clear sols which are much more sensitive towards electrolytes than the pure dye sols. With the amphoteric euglobulin one might, it is true, take into account the action of colloidal ions with opposite charges; various circumstances in the behaviour point, however, to an influence resembling that of tannin.

Albumin does not sensitize either the pure dye sol or the dye-globulin sol, but always protects both. There is thus an antagonistic behaviour between globulin and albumin: the former sensitizes and the latter protects. Brossa was able to show that this antagonistic relationship between globulin and albumin is also apparently of importance for their behaviour in the serum.

Page 589. In connexion with the theory of protective action, it is noteworthy that, according to Pauli,[2] many proteins exert no protective action on a gold sol which has been freed to the greatest possible extent from electrolytes. Hence, a certain content of electrolyte is necessary for the protective action of many (perhaps of all) protective colloids.

Page 605 *et seq.* The description of the properties of emulsions must be supplemented in various directions.[3]

The critical ratio of about 74 : 26 need not hold strictly for the ratio of disperse to continuous phase which is actually present. The considerations which led to this figure presupposed particles of the same size. If, in addition to the large particles, a sufficient number of small ones are also present, these might fill the interstices between the large particles in such a manner that the disperse phase formed a considerably larger fraction of the whole. We must further take into account the fact that the particles of the disperse phase, provided they are surrounded by a sufficiently tough protective envelope, need not maintain their spherical shape when pressed closely together.[4] If, however, one works with particles as uniform in size as possible and with protective envelopes which are neither too thick nor too solid, the above ratio appears to be satisfactorily fulfilled.[5]

[1] Kolloidzeitschr. **32**, 107 (1923).
[2] Kolloidzeitschr. **31**, 252 (1922).
[3] See also a comprehensive treatment of emulsions by *W. Clayton*: "The Theory of Emulsions and Emulsification." London, 1923: J. & A. Churchill.
[4] *Bancroft*, Journ. Phys. Chem. **16**, 179 (1912).
[5] *Bhatnagar*, Journ. Chem. Soc. **117**, 547 (1920).

The transition of an aqueous into a non-aqueous emulsion by the mere change of the emulsifying agent is remarkable, and is important in connexion with biological phenomena. Newman (cf. p. 605) had already found that, using sodium oleate, only an emulsion of benzene in water can be obtained; with magnesium oleate, on the other hand, one of water in benzene is produced; whilst a water-oil (the first word always refers to the disperse phase) emulsion can be transformed into an oil-water emulsion by addition of sodium oleate. Clowes,[1] who has investigated this subject in more detail, found that soaps of the alkali metals behave like sodium oleate, whilst Ca, Sr, Ba, Al, Fe salts resemble the magnesium salt. When the electrolytes of the first and second kind are present in a certain critical ratio the tendency to form either type of emulsion is equally strong; a certain instability then prevails, since both types strive to appear in equal degree. The transition of the oil-water emulsion into the water-oil emulsion takes place in the following manner: the oil drops become elongated and unite to larger drops which enclose many isolated drops of water. These drops of water are also at first large and elongated, but subdivide into small spherical particles the more the critical point is overstepped. The small oil drops which at first remain distributed in the separated water drops then also disappear. Bhatnagar [2] has confirmed these results and extended them to cases in which proteins or coarsely disperse oxides, etc., served in place of soaps as emulsifying agents. A reversal of the emulsion was also observed in these cases; in every case OH' and PO_4''' ions favoured the formation of the oil-water emulsion, whilst salts of the heavy metals favoured that of the water-oil emulsion. Table 195 gives a summary of his results.

TABLE 195

Reversal of an Emulsion by Electrolytes

Emulsifying Agent.	Electrolyte causing Reversal.	Original Type of Emulsion.
Na oleate	Salts of Ca, Ba, Sr, Al, Fe, Cr, Zn, Cu, Ni	Oil in water
Casein	,, Al, Fe, Th. Acids	,, ,, ,,
Lecithin	,, Al, Fe, Th	,, ,, ,,
Resin	KOH, K_3PO_4	Water in oil
Carbon	KOH, K_3PO_4	,, ,, ,,
$Zn(OH)_2$ in neutral solution	KOH, K_3PO_4	,, ,, ,,
$Zn(OH)_2$ in alkaline solution	Salts of Al, Th. Acids	Oil in water
$Al(OH)_3$	KOH, K_3PO_4	Water in oil
PbO	KOH	,, ,, ,,

Clowes and Bhatnagar consider that this behaviour is caused, in particular, by two influences: firstly by the hydrophily or hydrophoby of the colloidally or coarsely disperse particles of the emulsifying agent, and secondly by their charge, which is produced by a preferential adsorption of anions or cations. Oil-water emulsions are formed when the emulsifying agent is hydrophilic and its charge preferentially negative; water-oil emulsions when the emulsifying agent is hydrophobic and its charge preferentially positive. Considerable support for this view is given by the fact that, for example, Ca, Sr, and Ba oleates are hydrophobic, hence pass preferentially into

[1] Kolloidzeitschr. **15**, 123 (1914); Journ. Phys. Chem. **20**, 407 (1916).
[2] Journ. Chem. Soc. **117**, 542 (1920); **119**, 61, 1760 (1921).

the oil phase and thereby promote the formation of the water-oil emulsion.

Clowes discusses in detail the importance such relations may have for the comprehension of the cell wall and its permeability. The cell wall consists, perhaps, of a lipoid-water emulsion, the permeability of which undergoes fundamental changes according to the concentration of the ions acting on it, so that it might consist of a water-oil or an oil-water emulsion. Its permeability for dissolved substances could be very different.

Emulsions in which the one liquid forms only thin intermicellar lamellæ between the drops of the other liquid are termed by Rhumbler [1] *spumoids*; they show, especially when the intermicellar liquid is viscous, a strong resemblance to foams; this is particularly apparent in their resistance to mechanical and similar actions (cf. p. 797). Rhumbler showed, in a series of experiments, how similar is the behaviour of such spumoids to that of protoplasm. As an example of a spumoid he employed a structure first prepared by Bütschli.[2] Viscous, partly oxidized olive oil was ground with finely powdered K_2CO_3. A foam of fine drops in a skeleton of olive oil was thus formed.

It may be further mentioned that the change of the one type of emulsion into the other may be readily followed by means of the conductivity [3]; this is far greater with oil-water emulsions than with water-oil emulsions. Further, using nitrocellulose as emulsifying agent, an emulsion of water in organic liquids may be prepared; an adsorption of nitrocellulose at the surfaces of the particles may be demonstrated in such emulsions.[4]

Page 613. Radium radiation may also be mentioned among the influences which produce the denaturing of protein sols. Fernau and Pauli [5] have found that albumin in a solution containing salt is denatured under, for example, conditions similar to those in the case of a CeO_2 sol (cf. p. 485). The coagulation temperature of the irradiated solution is lower; it is also precipitated more readily by alcohol.

Page 614. The great similarity between the behaviour of fibrin and V_2O_5 sols has recently been tested and confirmed by Wiegner.[6]

Page 658 *et seq.* The data which have meanwhile been collected concerning the structure of gels favour, in principle, the micellar theory of Nägeli and Zsigmondy. But the presence of thread-like structures, formed by the association of the micellæ, must be assumed far more generally than has been done in the treatment on p. 659 *et seq.* These threads traverse the gel in the form of a network and cause the cohesion and great elasticity which distinguish gels from sols. Even the experiments of Zsigmondy and of Flade (cf. p. 724) on gels of soaps and of barium malonate can be interpreted in this way; McBain,[7] Barrett,[8] Bogue [9] and others have also come to this view.

[1] "Methodik d. Nachahmung von Lebensvorgängen durch physikalische Konstellationen." "Handbuch d. biolog. Arbeitsmethoden von Abderhalden," Abt. V, Teil 3, Heft 2, p. 219 (1921).

[2] "Untersuch. über mikrosk. Schäume u. d. Protoplasma," Leipzig, 1892. Further *Strümpell* and *Koch*, "Elemente d. Tierphysiologie," p. 65, Jena, 1916.

[3] *Clayton*, Brit. Ass. Coll. Rep. **2**, 114 (1918); *Bhatnagar*, Journ. Chem. Soc. **117**, 542 (1920).

[4] *H. N. Holmes* and *D. H. Cameron*, Journ. Amer. Chem. Soc. **44**, 66 (1922).

[5] Kolloidzeitschr. **30**, 6 (1922).

[6] *Wiegner, Magasanik* and *Gessner*, Kolloidzeitschr. **30**, 145, 1922.

[7] Miss *Laing* and *McBain*, Journ. Chem. Soc. **117**, 1506 (1920); *Darke, McBain* and *Salmon*, Proc. Roy. Soc. **98**, A, 395 (1921).

[8] Biochem. Journ. **14**, 189 (1920); Kolloidzeitschr. **28**, 217 (1921).

[9] Journ. Amer. Chem. Soc. **44**, 1343 (1922).

Page 685. That a liquid which is distributed in the capillary spaces of a fine powder has a lower freezing-point than a liquid in mass follows from measurements by Parker.[1] He obtained depressions of the freezing-point which reached 2° and over not only with powders of ferric oxide and silicic acid in water but also with powders of aluminium oxide and silicic acid in benzene, etc. The latter experiments are particularly conclusive since there is no possibility of the solid dissolving in the liquid and so vitiating the results.

Page 687. The adsorption of ammonia by silicic acid has been explained by Davidheiser and Patrick.[2] One must take into account not only an adsorption process, but also the solubility of the ammonia in the water of the gel and a reaction with the acid residues which are always contained in the gel.

Page 690. The experiments briefly described on this and other pages (cf. pp. 268 *et seq.* and 700) have meanwhile been extended and summarized by J. Loeb.[3] The following may be considered a summary of the purely experimental results. When the influence of the $H^{\cdot}$ ion concentration is taken into account in Loeb's manner, and this is unquestionably justifiable, indeed necessary, with substances, such as the proteins, which are so sensitive to $H^{\cdot}$ ions—it is found that a decided parallelism exists between the dependence both of the osmotic pressure and of the swelling of the protein, on the $H^{\cdot}$ ion concentration. When one works, in this manner, with $H^{\cdot}$ ion concentrations as comparable as possible, the significance of the lyotropic series of ions becomes greatly obscured; this is, in fact, the case not only with respect to the osmotic pressure but also to the salting-out of the proteins. It is quite clear that the E.M.F. of cells in which collodion membranes containing a solution of a protein in hydrochloric acid and dipping into a pure solution of hydrochloric acid is interposed between two normal electrodes, may be calculated according to Donnan's theory (cf. p. 561), and that this can be done in a similar manner with cells of Beutner's type (cf. p. 277) in which a layer of swollen gelatin between solutions of electrolytes serves as intermediate phase. The distribution coefficient of the ions is no doubt decisive both for the Donnan membrane equilibrium and for Beutner's cells.

Loeb not only seeks to explain the above-mentioned parallelism between osmosis and swelling and, in general, the influence of electrolytes on protein solutions, on the basis of Donnan's membrane equilibrium, but wishes to generalize and to apply these views to all sols, even to the hydrophobic ones,[4] which appears to me objectionable and unsuitable. He obtains, for example, the relation between osmosis and swelling from the point of view[5] that, just as in osmosis the large protein ion is unable to pass through the membrane, so in swelling it is unable to pass from the gel into the liquid owing to the cohesion of the protein gel; hence the water penetrates into the gel during swelling just as it penetrates through the membrane in osmosis. The extensive similarity between swelling pressure and osmotic pressure has already been discussed on p. 677; at the same time, however, the chief difference between them was also pointed out. The same con-

[1] Journ. Amer. Chem. Soc. **43**, 1011 (1921).
[2] Journ. Amer. Chem. Soc. **44**, 1, 1922.
[3] "Proteins and the Theory of Colloidal Behaviour." New York, 1922: McGraw-Hill Book Co., Inc.
[4] I should not consider the hydrophobic character of a casein sol, which he has chosen as an example, as at all pronounced.
[5] *Procter* [Journ. Chem. Soc. **105**, 313 (1914)] and *Procter* and *J. A. Wilson* [*ibid.* **109**, 307 (1916)] have already discussed these views.

siderations also apply here. It may be further recalled that Flusin (cf. p. 696) likewise found a connexion between osmosis and swelling with caoutchouc in organic liquids ; in this case there is no question of an effect of ions. The parallelism observed by Loeb probably simply depends on the fact that the affinity of the protein ions for water takes effect both in osmotic phenomena and in swelling.

I cannot conceive how the exceedingly diverse phenomena which occur in the coagulation of genuine hydrophobic sols [gold sols, v. Weimarn's sulphur sols, etc. (cf. p. 415 *et seq.*)] can be explained on the basis of Donnan's membrane equilibrium. It appears to me, indeed, desirable to submit Loeb's theory to a more rigorous test with protein sols in the direction, for example, of Kruyt's experiments on p. 833.

Page 692. A thorough investigation by Schade and Menschel [1] shows that the œdema in heart and kidney diseases cannot be explained by a swelling produced by acidification. Of the evidence against this view, only the following need be mentioned : The œdema in the cases mentioned depends on a collection of water in the connective tissue ; under body conditions, however, acids cause the connective tissue to shrink and not to swell. Further, a determination of the $H^{\cdot}$ ion concentration shows that the œdema in the living organism is not acid.

Page 711 *et seq.* Kohlschütter [2] has already thoroughly investigated similar reactions, in which disperse structures are formed from coarsely crystalline substances, for example the formation of $Al(OH)_3$ from various aluminium salts, and of $Cu(OH)_2$ from various copper salts. He terms such processes *topochemical*, since in these cases the local conditions which are important for the formation of the hydroxides are provided by the definite positions of the metallic atoms in the space lattice. According to the experimental conditions and the initial substances, hydroxides of very different degrees of dispersity were obtained ; and, for example in the experiments with Cu salts, it was observed that the degree of dispersity increases with the true molecular volume of the initial substance. According to Kohlschütter and Stack,[3] such topochemical processes are also important in the formation of macroscopic crystals in sols and gels.

Page 724. A few more gels may be mentioned in which thread-like particles have been observed either microscopically or ultra-microscopically or whose presence has been rendered probable in other ways, especially on the grounds of double refraction. In the first place there are the jellies of Li-urate,[4] the behaviour of which as well as of gels of Na urate (see Schade) [5] recall strikingly that of soap gels. To these gels belong further those of dibenzoyl-*l*-cystine [6] and of various salts of quinine and its derivatives, especially of eucupine acetate.[7]

Page 727. The small degree of uniformity is likewise revealed in the experiments of Seifriz, alluded to on p. 832, in which the attraction of a

[1] Kolloidzeitschr. **31,** 171 (1922).

[2] Zeitschr. f. anorg. u. allg. Chem. **105,** 1 (1918) ; *Kohlschütter* and *Tüscher, ibid.* **111,** 193 (1920) ; *Kohlschütter* and *Sedelinovich,* Zeitschr. f. Elektrochem. **29,** 30 (1923) ; *Kohlschütter* and *Roesti,* Ber. d. deutsch. chem. Ges. **56,** 275 (1923).

[3] Zeitschr. f. Elektrochem. **28,** 554 (1922).

[4] *Keeser* and *Zocher,* Kolloidchem. Beiheft. **17,** 189 (1923).

[5] Zeitschr. f. kliń. Medizin, **93,** 1 (1922).

[6] *Gortner* and *W. F. Hoffmann,* Journ. Amer. Chem. Soc. **43,** 2199 (1921) ; *C. G. L. Wolf* and *Rideal,* Biochem. Journ. **16,** 548 (1922).

[7] *Rona* and *Takata,* Biochem. Zeitschr. **134,** 97 (1922), and unpublished experiments by *Rona, Schmerl* and *Zocher.*

nickel particle by the point of a magnet is followed under the microscope. This behaviour can also be seen macroscopically in the following manner: A round shot falls through a gelatin gel, and even through a concentrated gelatin sol, irregularly and haltingly, and not smoothly as it does through glycerine; the path of fall, once produced by the shot, is evident for a long time in the fact that the shot will traverse it in much shorter time than any other path.

Page 732 *et seq.* Among the numerous investigations of Liesegang's rings prominence may be given to that of Bradford,[1] which appears to me to signify an important advance for the theory of this process. It introduces a factor not hitherto considered, namely the adsorption on the precipitated particles of the rings of substances originally present in the gel in great dilution. Hence he assumes that, immediately the precipitate is formed, its surroundings are depleted both of the substance ("reagent") diffusing inwards and of that ("dissolved substance") present in the gel. This depletion is the more pronounced since an adsorption by the separated particles may be assumed; its influence will be particularly evident in the case of the "dissolved substance," which is present in smaller concentration.

At their surfaces, the particles are in equilibrium with a solution which corresponds to the solubility product. The depletion might proceed so far that, in the extreme case, the concentration of the "dissolved substance" in the surface is an adsorbed amount, which is naturally in equilibrium with a much smaller concentration in the solution. When the reagent diffuses past the layer, it first reaches a region in which not only is the rate of formation of nuclei below the maximum, but the concentration is below the solubility product. Only at an appreciable distance from the layer is the concentration of the "dissolved substance" again sufficiently large in order to attain the solubility product.

The appearance of rings in general may be thus understood. It is also intelligible that they appear preferentially with the finest possible crystals and with amorphous precipitates; the surface is then large and the adsorption strong. Further, it explains the influence of the nature of the gel. If this diminishes the size of the granules, that is, increases the rate of formation of nuclei and diminishes the crystallization velocity, rings are obtained (silver chromate in gelatin); if it diminishes the rate of formation of nuclei whilst the crystallization velocity remains large, no rings are formed (silver chromate in agar). It is clear that every circumstance which influences the coagulation or peptization of the particles will also influence the formation of rings.[2] One can, for example, also understand that, in the separation of gold in gels, bands appear in which finely and coarsely disperse layers alternate. The finely disperse ring which separates first causes a strong adsorption. As a result the concentration of the gold salt becomes so small that only a small number of nuclei are formed in the next ring, and these have time to grow to larger particles. The coarser particles adsorb to a smaller degree, the concentration of the gold salt remains higher, and hence the number of nuclei is again larger so that the next ring is again finely disperse. Further, Bradford was able to demonstrate directly an adsorption of the "dissolved substance" by the particles of the rings.

His objections to a view discussed by M. H. Fischer and McLaughlin [3]

[1] Biochem. Journ. **10,** 169 (1916); **11,** 14 (1917); **14,** 29, 474 (1920); Kolloidzeitschr. **30,** 364 (1922).

[2] See *Chatterji* and *Dhar,* Kolloidzeitschr. **31,** 15 (1922).

[3] Kolloidzeitschr. **30,** 22 (1922).

appears to me to be justified. These authors assumed that the formation of rings might have the following cause. The finely disperse precipitate at first formed may at the commencement be semi-permeable and so prevent the further diffusion of the reagent. In time, the precipitate coarsens and allows the reagent to pass through, which then produces a new ring at a certain distance from the old one. Against this, Bradford emphasizes that it is not clear why the solubility product is not reached directly at the ring immediately this has become permeable, and why the particles of the first ring cannot then act as nuclei and simply cause a uniform growth of the rings in the direction of a diffusion.

Of isolated investigations may be mentioned the imitation of agates by Bhatnagar and Mathur [1] on the basis of Liesegang's rings in silicic acid jellies, and the curious observation by E. Karrer [2] that the reaction product formed by the interaction of gases diffusing into one another in a tube also separates on the walls in the form of rings ; this was observed in the interaction of NH_3 and HCl in the presence of moisture.

Page 754. Clear experiments on the effect of salts in dyeing with substantive dyes originate from F. Auerbach.[3] They have an unfavourable action when they coagulate the dye in the bath, and a favourable one when they produce this effect in the fibres ; hence an optimum salt action occurs, which can be demonstrated. In agreement with this view, the optimum in the case of a negative dye sol is displaced towards smaller and smaller concentrations the greater the coagulating action of the cation of the salt employed.

Page 760. Willstätter [4] has recently utilized adsorption to a large extent for synthetic purposes, especially for the purification of enzymes. It is manifestly particularly suitable for this purpose, for it constitutes an extremely mild method by which unstable substances can be removed from mixtures and again obtained, in the greatest possible degree unchanged, by washing the adsorbent with suitable solvents. The method is also fairly flexible. Not only can different solvents and positive or negative adsorbents be employed, but the adsorbability of the enzyme, and the possibility of removing it from the adsorbent by washing, are strongly influenced by foreign substances. Since enzymes are initially very impure, no conclusion as to their acidic or basic nature can at first be drawn from their adsorbability. Thus, the statement on p. 760 that invertase is always negative and hence is not adsorbed by negative kaolin, is, according to Willstätter, incorrect. If invertase is to a large extent freed from impurities by treatment with $Al(OH)_3$ and removal by washing, it is then also smoothly adsorbed by kaolin. Willstätter and Kraut [5] have compared a series of Al_2O_3 preparations, prepared in different ways, with respect to their adsorptive power for invertase and have found that this does not depend alone on the degree of dispersity but also on the specific properties of the adsorbent.

A series of useful terms have been introduced by Willstätter. He gives to the compound of adsorbent and adsorbed substance the name *adsorbate*, employs the expression *elute* for the process of removing the adsorbed substance by washing, and designates by the name *co-adsorbent* a substance

[1] Kolloidzeitschr. **30,** 368 (1922).
[2] Journ. Amer. Chem. Soc. **44,** 951 (1922).
[3] Kolloidzeitschr. **30,** 166 (1922).
[4] In particular *Willstätter,* Lieb. Ann. **422,** 47 (1921) ; *Willstätter* and *Racke, ibid.* **425,** 1 (1921) ; **427,** 111 (1922).
[5] Ber. d. deutsch. Chem. Ges. **56,** 149 (1923).

which influences the adsorption, and by *co-eluent* one which influences the washing process.

Page 768. The conjecture put forward on this page that, in the poisoning of serum lipase by foreign substances, the abnormal dependence on the concentration depends on the environment in which the reaction takes place, has not been confirmed. According to Rona and Pavlović[1] liver lipase shows a similar curious dependence on concentration when poisoned by atoxyl, although it acts under conditions quite different from those of serum lipase. According to the investigations of Rona [2] and his collaborators one must rather reckon with characteristic differences even with ferments which one would at first be inclined to regard as related. Thus, serum lipase is poisoned strongly by quinine according to the concentration function just mentioned. Liver lipase is not sensitive to quinine ; pancreatic lipase is sensitive and the adsorption function resembles the adsorption isothermal, but the taking up is not reversible nor is the equilibrium established smoothly ; stomach lipase is likewise sensitive, the adsorption isothermal also holds, but the equilibrium is established rapidly and reversibly. In pathological cases one can immediately infer the presence of liver lipase in the blood if the lipase action of the serum remains even in the presence of large concentrations of quinine.[3]

Page 777. In view of the importance which the polarization of the Tyndall light emitted by gas molecules has for the theory of the structure of molecules,[4] the careful investigation of this phenomenon by Rich. Gans [5] may be pointed out.

Page 781 *et seq.* The comprehensive treatment by Bär [6] of the determination of the elementary quantity of electricity on the basis of the behaviour of mist particles may, in the first place, be pointed out. Further, departures from normal behaviour appear, as is well known (cf. p. 782), immediately the particles exceed a certain size. Regener (cf. p. 782 *et seq.*) explained this on the grounds that it is necessary to consider, not only the departure of the particles from spherical form, but also a condensation of gas on their surfaces, which, especially with small particles, would take effect and falsify their density. Hence, with a strongly adsorbed gas, departures from normal behaviour should occur with particles of a larger diameter than in the case of a weakly adsorbed gas. M. König [7] was able to confirm this conclusion. With small drops of mercury, departures already occurred at a radius of 210 $\mu\mu$ in the strongly adsorbable carbon dioxide, but not until one of 120 $\mu\mu$ in dry air.

Page 794 *et seq.* The peculiar relations which exist with these soap lamellæ are, according to an investigation by Perrin,[8] far more diverse than appears from the description of earlier observers. Johonnott [9] mentioned incidentally that he had not only found two black spots but had been able to count up to five. Perrin has also met with five, and he likewise gained the impression that they intermittently pass into one another. He obtained

[1] Biochem. Zeitschr. **130,** 225 (1922).
[2] *Rona* and *Pavlović*, Biochem. Zeitschr. **134,** 108 (1922) ; *Rona* and *Takata*, *ibid.* **134,** 118 (1922).
[3] *Rona*, *Petow* and *Schreiber*, Klin. Wochenschr. **1,** 2366 (1922).
[4] See for example *Born* and *Gerlach*, Zeitschr. f. Physik, **5,** 374 (1921).
[5] Ann. d. Phys. (4) **65,** 97 (1921).
[6] Ann. d. Phys. (4) **67,** 157 (1922).
[7] Zeitschr. f. Physik, **11,** 253 (1922).
[8] Ann. d. Phys. (9), **10,** 160 (1918) ; further, *Wells*, *ibid.* (9), **16,** 69 (1921).
[9] Phil. Mag. (6), **11,** 751 (1906).

a still more general formation of strata by colouring the lamella with a fluorescent dye, such as fluorescein or æsculin, and then illuminating it. Between 0 and 210 $\mu\mu$ he was able to detect up to 38 faces of different colour. Of these, the first five were black ; the remainder had the colour of thin films and could be sharply distinguished from one another. His experiments indicate so far that each face consists of overlaying films, each single film having a thickness of about 5 $\mu\mu$. The thinnest black spot would then correspond to one single film of this kind, for its thickness amounts, according to Johonnott and Rickenbacher (cf. p. 796), to 6–7 $\mu\mu$. Perrin also came to the result that this black spot and, quite generally, the surfaces of soap-water lamellæ, have a composition different from that of the mass of the liquid. He succeeded in demonstrating that when a soap solution is allowed to foam, and the foam is then removed, it gives, in contrast to the remaining liquid, an acid reaction. He would like to assume an adsorption layer of oleic acid two molecules in thickness. I should prefer, with McBain, to consider a layer of the colloidal particles of an acid soap (cf. p. 832).

Perrin observed a formation of strata, similar to those of soap solutions, with solutions of gamboge and colophony.

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